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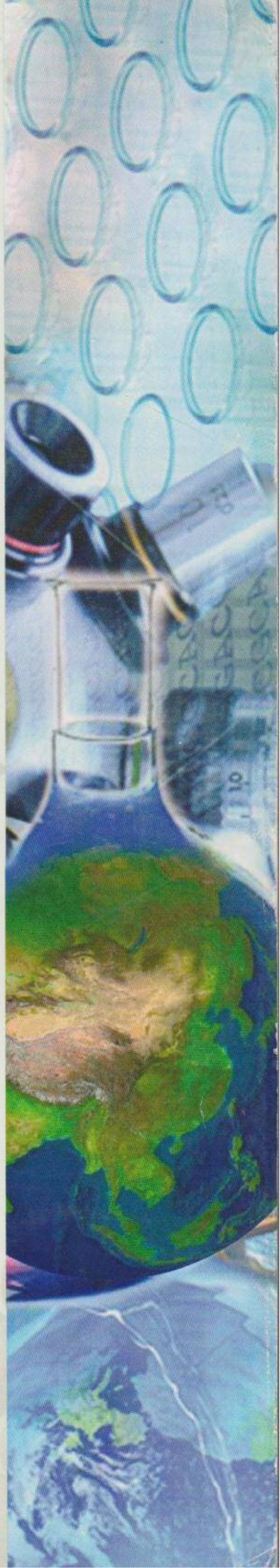
The 17th Regional Symposium on Chemical Engineering



Book of Abstracts

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ANALYSIS TECHNO-ECONOMIC OF PRODUCING SYNGAS BY USING VARIOUS METALLIC CATALYSTS IN STEAM REFORMER OF PUSRI II PALEMBANG

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Abstract

Nickel as economical catalyst has been used in various process application. One process application that uses this catalyst is the steam reformer in PT PUSRI II Palembang, Indonesia as part of an overall process to produce syngas from natural gas. Through nickel catalyst, the conversion of steam reformer is definitely high, but large amount of fuel to increase the steam reformer temperature is needed and the catalyst easily deactivates with sulfur and high temperature. Techno-economical analysis assessments highlight the various technological possibilities and economic aspects involved in the production of syngas. This method has been done at the steam reformer part of PT PUSRI II Palembang, in this research aimed to investigate the comparison of catalysts performance of platinum, palladium, cobalt, and nickel to syngas conversion. Various catalysts Pt/Pd/Co/Ni are the variable of the research for the techno-economic analysis, which consisted of operating condition, catalyst volume and price, fuel economization and syngas conversion. Trough techno-economic analysis, platinum was found to give the best results in analysis compared with others, giving low process temperature, catalyst volume used, fuel economization and high syngas conversion of up to 61 % at 653 K.

Introduction

In some of petroleum and chemical industries needed a large quantity of hydrogen. The largest application of hydrogen is in the processing of fossil fuels, and production of ammonia. In ammonia production, syngas has important role in whole processes, as a intermediate product to other utility. Steam reforming technology used for reforming process, which is composed mainly of methane to produce syngas. Other components are like ethane, propane and butane will disrupt conversion, which causes reduction in product conversion.

Pusri use steam reforming in producing syngas, where efficiencies up to approximately 85 %, give the highest conversion with simple technology than others. Research of steam reforming technology in producing syngas has been developed since 1930s. Actually, nickel used as catalyst and reacted at 815 ^{0}C and 35 atm and the highest conversion attained was 40 %.

Borowiecki and Barcicki (1979) has been studied about the activity and selectivity of the methane steam reaction in a gradientless reactor at atmospheric pressure and 700 – 850 ^{0}C. Various catalyst used in the reaction was nickel, platinum, palladium, ruthenium and irridium. The results obtained were for Pd and Rh catalyst, much higher CO amounts were abserved than for Pt and Ir.

Setzer (1988) researched about activity sulfur tolerant for some catalysts of steam reforming. They are nickel, iridium, palladium and platinum. The results show that the order of activity proceeds from palladium to iridium to platinum with all providing higher activity than the commercially available catalyst. When compared to the improved nickel and rhodium catalysts, palladium is between and platinum display significantly higher activity.

The purpose of this research was to study and discuss about performance of various catalysts in steam reforming with compared to nickel catalyst to conversion syngas. This research used technoeconomic analysis to compared catalysts in energy consumption to conversion of syngas.

Material

The steam methane reforming process is characterized by multiple-step and severe reaction conditions in the presence of a metal-based catalyst (nickel). The reaction between natural gas or other light hydrocarbons and steam results in a mixture of hydrogen, CO and CO_2 :

$CH_4 + H_2O \rightleftharpoons CO + 3H_2$, $H_1 = 206$ kJ/mol (1)

$CO + H_2O \rightleftharpoons CO_2 + H_2$, $H_2 = -41$ kJ/mol (2)

Endothermic steam reforming of hydrocarbon requires an external heat source, so temperature must be above ~780 ^{0}C for the reaction to proceed at a reasonable rate. It causes energy consumption will increase in line with fuel requirement. With use catalyst, temperature reaction become lower and energy consumption will decrease. Nickel catalysts suffer from catalyst deactivation by coke formation more severely when higher hydrocarbons are reformed at low steam/carbon ratio (Rakass, 1975). Many other metal used as catalyst in reaction, like noble metal (cobalt) and precious metal (rhodium, platinum, palladium).

Group VIII metals possess much higher catalytic activities than nickel, their use has not gone beyond the range of assays beside their higher activity, resistance to coking and thermostability much better than Ni. Each metal has different influence to the reaction. Generally, the catalyst will have high strength to reach equilibrium reaction faster so the conversion also higher than others. Although precious metals such as Pd, Pt and Rh are more stable and active for steam reforming of hydrocarbons.

Technoeconomic analysis is to assessment highlight the various technological possibilities and economic aspects involved in syngas production. In technoeconomic analysis, it is considered not only product conversion but also benefit or not for industry. Hence, alternative catalyst needed to give high conversion with lower operational cost.

Experimental

This research used various catalyst metal except nickel in steam reforming process. Steam reforming reaction take place in reformer tube, both of inner and outer tubes are filled with a porous catalyst structure. Inside the reactor tubes, there are two reaction occure : the methane steam reformer and water gas shift reaction.

According to thermodynamics, two of reaction are both equilibrium reaction with a forward and backward reaction rate. The ratio in reaction dependent of temperature, can be calculated the speed reaction are equal. For the reaction, the two following equilibrium constants can be formulated:

$$K_{p1}(T) = \frac{[CO][H_2]^3}{[CH_4][H_2O]} \qquad (3)$$

$$K_{P2}(T) = \frac{[CO_2][H_2]}{[CO][H_2O]} \qquad (4)$$

The Van't Hoff equation calculates the value of each Kp as a function of temperature:

$$K_P = K_{P,298} \exp\left(\frac{\Delta H}{R}\left[\frac{1}{298} - \frac{1}{T}\right]\right) \qquad (5)$$

The reaction kinetics calculates speed at which the reaction occurred, when the rate of reactions has different value with the different catalysts. For the calculating rates of reactions with the Arrhenius depend on temperature:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \qquad (6)$$

From this equation, derivable become:

$$LnK = Ln\ A - \frac{Ea}{R} x \frac{1}{T} \qquad (7)$$

Where A as pre-exponential factor and Ea is the activation energy in J/kmol. The value of Ea is given by Arrhenius graph, where reaction rate constant k is plotted of absolute temperatures.

For determining change operation condition and volume various catalysts used by equation below:

$$V = \left(\frac{Fa0}{k} x\ Ca^2\right) x \left(\frac{1}{M-1}\right) x \left(\frac{Ln\,(M-X)}{M\,(1-X)}\right) \qquad (8)$$

Where V is volume of catalyst, Fa0 is volumetric flow rate, k is rate constant of

reaction, Ca is methane concentration, M is ratio steam to methane and X is conversion value.
Economical aspect becomes important to be considered base on economical principle. That principle is gain largest profit by smallest production cost.

Results and Discussion

The kinetic variables as the object of this research were various catalyst, include of platinum, palladium, cobalt to nickel. This research comprised effect of catalysts to change operation condition, volume of catalyst, catalyst price, fuel economization and also syngas conversion.

Effect of operation condition change with different catalyst.

As nickel has many disadvantages, there are some metal that used as alternative catalysts in steam reforming process. Figure 1 depicts operation condition was changed in different catalyst. It was found that when reactivity of catalyst was increasing, the temperature to reach maximum operation condition became lower than used.

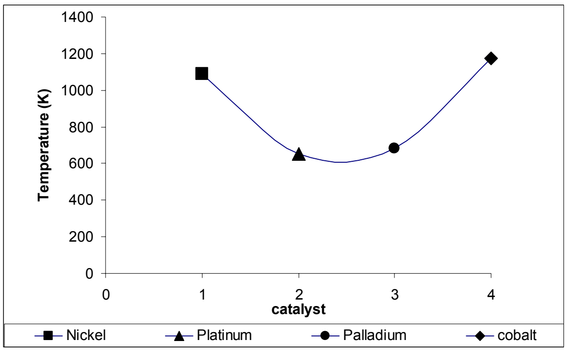

Figure 1. Effect of change operation condition with different catalyst

Generally, catalyst reactivity has higher influence to the operation condition in steam reforming process. The catalyst which has more electronegativity and reactivity will enable to reach equilibrium reaction faster or rate of reaction will faster, so the temperature and enthalpy reaction has decrease compared with catalyst which has low catalytic activity.
From this figure, it will seen that platinum has the minimum temperature than others to reach equilibrium reaction, that is 653 ^{0}K. It is caused by the total energy of reaction decreasing in line with reduction of temperature reaction.

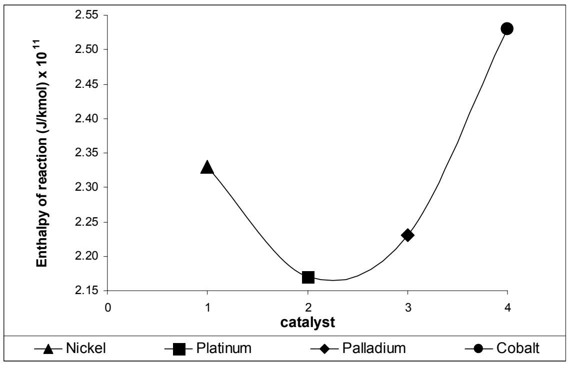

Figure 2. Value of enthalpy reaction for various catalyst

Value of enthalpy reaction in fig 2 shows that platinum catalyst has a lowest enthalpy reaction, that is 2, 17 x 10 ^{11} J/kmol. It will be understand that a very active catalyst will make the reaction faster than others so equilibrium will be reach with a little energy of reaction.

Effect of various catalyst to catalyst volume.

Influence of catalyst volume to the rate of reaction is shown in fig 3. When the catalyst reactivity has increase, the equilibrium reaction will be reached quickly. It will caused that total catalyst for reaction lower than catalyst which has a low reactivity to get the maximum conversion. The indicator to the rate of reaction is rate constant of reaction. If the constant of reaction is high, the result is volume of catalyst needed small, because the activation energy in reaction also small.

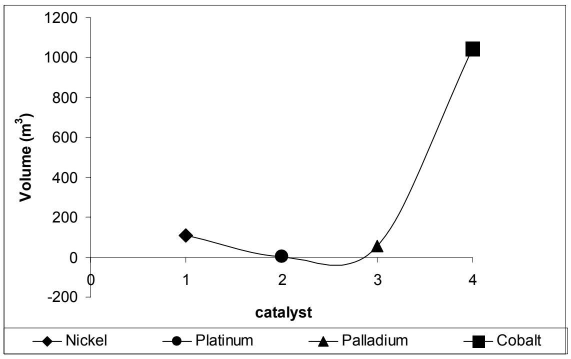

Figure 3. Effect of various catalyst to the catalyst volume

From this figure, the catalyst volume has the smallest value if the reaction use platinum catalyst, that is 1,27 m^3. It's mean that the reaction will be fastest than another catalyst and also produce high efficiencies in syngas production.

Techno-economic analysis of steam reforming catalysts.

1. Price level in some of catalysts.

Catalyst has important role in accelerating rate of reaction to reach the equilibrium reaction be faster with uses catalyst, so will give some opportunities in reaction. Now, catalyst in PT Pusri has some challenges, it is easily deactivates because of sulfur poisoning or carbon formation as result of high temperature and causes sintering in catalyst. But, for precious metal, actually has catalytic activity and stability higher than noble catalysts and resistance to sulfur content that enhance the conversion of product.

Beside high conversion level, catalyst price is consider as important factor in steam reforming. Economic principle to get high profit with low operational cost still considered as important thing in industry. From the figure 4 below, it could be seen that platinum catalyst has the minimum price than others, except nickel catalyst. It will be happened because influence of volume catalyst that used in reaction. Low catalyst volume has influence to decreasing the price of catalyst. On the contrary, although the price of catalyst low, but if the catalyst volume used is high, it will increasing the total of catalyst price.

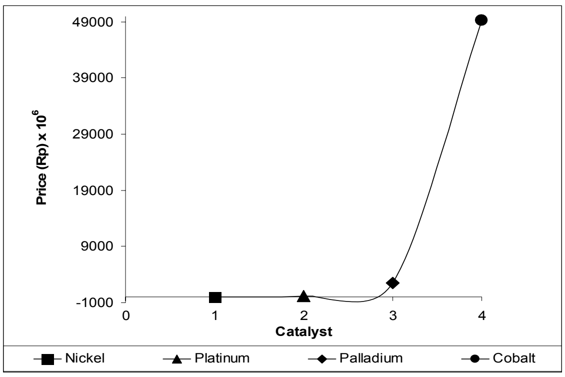

Figure 4 Price level of some catalysts

The lowest price of catalyst is nickel catalyst and followed by platinum catalyst. But, platinum catalyst better than others, especially for rate of reaction, high activity including temperature, activation energy , volume and also stability, the conclusion are high catalyst price will proportional with product level and energy consumption.

2. Analysis of fuel economization in reaction with variation of catalyst.

Fuel is important thing that influence overall of reaction. Fuel in steam reforming is natural gas in certain quantity. To get the high conversion of product, fuel was needed in high volume, causes the cost of syngas production will be expensive. With use catalyst, reaction occur faster in lower temperature and reducing to energy consumption. It is mean that industry will get high profit in line with increasing of efficiency.

Figure 5 shows fuel economization from different catalyst in reaction. From that figure, platinum catalyst produces high fuel economization than others. It is because of the high activity and stability of platinum causes the reaction taking place in lower temperature and make decreasing in fuel economization, which is Rp 286 billion/year. If the fuel economization is high, high reduction occurs in production cost and industry will get high profit from this.

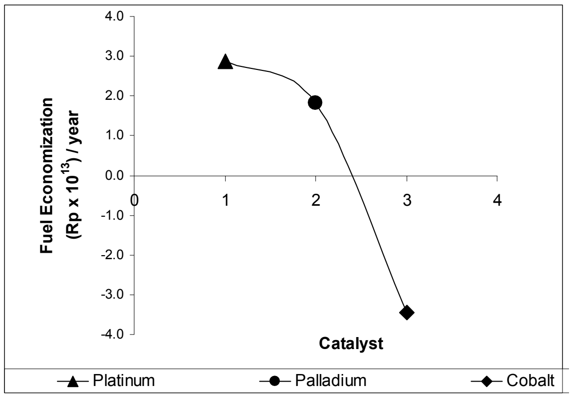

Figure 5 Fuel utilization with variation of catalysts

Analysis of yield syngas comparison with several catalysts

Catalyst has powerful effect to the yield product or conversion. Generally, yield syngas will be increased with catalytic activity of catalyst. If the reaction occur faster and reach the equilibrium reaction faster than reaction that using nickel catalyst, will resulting high yield product from steam reforming process.

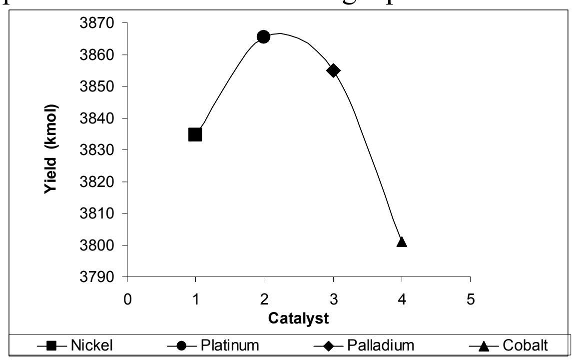

Figure 6 Yield product from several catalysts

From figure 6, it explains that platinum catalyst could giving the highest yield product, that is 3045, 446 kmol. It is mean that increasing of catalytic activity causes the rate of reaction become faster and also increasing of yield product. High catalyst activity accelerating speed of reaction until equilibrium and automatically yield of product higher than reaction with lower in speed of reaction.

Analysis of Conversion value of some catalysts

Catalytic reaction has many advantages, that is reaction will occur faster with low activation energy of reaction, like temperature of reaction, entalphy and fuel consumption will be lower than reaction non catalytic. Beside that, catalyst needed insignificant amount because of high value of catalytic activity catalyst.

If the reaction becomes faster to reach the equilibrium reaction, the value of conversion product will also higher. It is because the rate of reaction has proportional with conversion product of reaction.

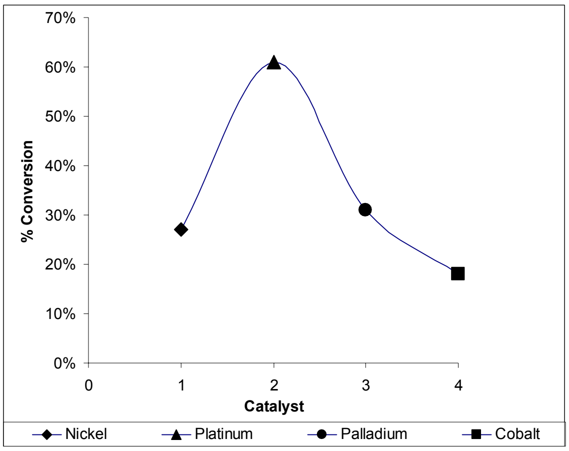

Figure 7 Conversion Value of some catalyst

From this figure, the highest value of conversion obtainable with uses platinum catalyst, which is 61 %. It is depend of constant rate of reaction, where if the rate of reaction was high, the reaction will reach equilibrium quickly and increase the conversion value of reaction.

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