CHEESA: Chemical Engineering Research Articles
ISSN **2614-8757 (Print)**, ISSN **2615-2347 (Online)**
Available online at: http://e-journal.unipma.ac.id/index.php/cheesa

Research Article

Catalyst Lifetime Analysis for High-Temperature Shift Converter (104-D1) at Urea Factory

Analisis Katalis Lifetime pada High-Temperature Shift Converter (104-D1) di Pabrik Urea

Rahmatullah[1*)], Rizka Wulandari Putri[1)], Bobi Mahendra[1)], Hegar Tifal Arofi[1)], Cecep Sumiratna Hadi[2)]

[1)]Universitas Sriwijaya, Chemical Engineering Department, Indonesia
[2)]PT. Pupuk Sriwidjaja Palembang, Indonesia

Article History
Received: 21th Maret 2023; Revised: 08th November 2023; Accepted: 08th November 2023; Available online: 21th November 2023; Published Regularly: December 2023

doi: 10.25273/cheesa.v6i2.15986.76-84

*Corresponding Author.
Email: rahmatullah@ft.unsri.ac.id

Abstract

The High-Temperature Shift Converter (HTSC) (104-D1) is crucial for converting CO gas into CO_2 in the ammonia unit. This is vital as the presence of CO poses a potential threat to the catalyst in the ammonia converter. In addition, maintaining HTSC (104-D1) at optimal performance is crucial, and this is achieved when the percentage of CO outlet remains below 3.41 mol% on a dry basis. The performance of HTSC (104-D1) was influenced by operating conditions (pressure and temperature) and the ratio of steam to carbon. The increase in temperature leads to an increase in the reaction rate and a decrease in CO conversion due to a decrease in catalyst performance. Therefore, this research aimed to assess the performance of HTSC (104-D1) after the Turn-Around process, specifically focusing on the CO conversion results and operating conditions. The analysis compared actual HTSC temperature, pressure drop, and CO conversion with design data using regression equations. This method predicted a catalyst lifetime of approximately 4 years and 8 months post-Turn-Around.

Keywords: Catalyst lifetime; CO conversion; shift converter; Turn Around

Abstrak
High-Temperature Shift Converter (HTSC) 104-D1 memiliki fungsi untuk mengonversi gas CO menjadi CO_2 pada unit ammonia. Keberadaan CO dapat menjadi racun bagi katalis di ammonia converter. Performa HTSC (104-D1) dikatakan baik apabila persen CO outlet dibawah 3,41 mol% dry basis. Kinerja HTSC (104-D1) dipengaruhi oleh kondisi operasi (tekanan dan temperature) serta rasio steam to carbon. Peningkatan temperature di HTSC (104-D1) menyebabkan naiknya laju reaksi dan turunnya konversi CO karena kinerja katalis yang menurun. Penelitian bertujuan untuk mengetahui bagaimana kinerja dari HTSC (104-D1) setelah Turn Around (Penggantian katalis) berdasarkan kondisi operasi dan konversi CO. Analisa dilakukan dengan membandingkan suhu, penurunan tekanan, dan konversi CO dari data aktual dengan data desain menggunakan metode persamaan regresi untuk memprediksi lifetime katalis. Lifetime katalis HTSC diperkirakan dapat dipakai sampai dengan 4 tahun 8 bulan setelah Turn Around.

***Kata kunci**: Konversi CO; lifetime katalis; shift converter; Turn Around*

1. Introduction

The fertilizer business is a crucial strategic sector for enhancing a nation's economy by playing an important role in supporting increased agricultural production. Urea fertilizer is widely used in agriculture, and is a key product of PT. Pupuk Sriwidjaja Palembang is an Indonesian fertilizer industry offering a range of products including urea, NPK, and ammonia fertilizers.

Ammonia is generated through the reaction of nitrogen gas from the air and hydrogen derived from natural gas [1]. As a crucial raw material in urea production at PT. Pupuk Sriwidjaja, ammonia undergoes a multi-unit production process, namely feed treating units, reforming units, purification & methanation, as well as compression synlopp & refrigeration units [2]. The ammonia produced is then used as a raw material in the urea manufacturing process through its reaction with carbon dioxide (CO_2). The synthesis gas (syngas), which consists of a mixture of hydrogen and nitrogen gases, has a major effect on the production of ammonia. The production of synthetic gas occurs in two stages, namely in primary and secondary reforming, yielding hydrogen, CO, and CO_2 [3].

The synthesis gas purification process consists of three main parts. First, the conversion of CO into CO_2 in the shift conversion unit, second, the absorption of CO_2 by Benfield's solution in the CO_2 absorber. The third stage is the conversion of CO and CO_2 gas into methane gas in the methanator process unit. To optimize hydrogen yield and remove CO, synthesis gas will be supplied to the shift converter [4], where CO reacts with steam (H_2O) to form CO_2 and hydrogen in an exothermic and reversible process, as shown in the following reaction.

$$CO_{(g)} + H_2O_{(v)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

In the shift converter, the reactions are both exothermic and reversible [5]. According to the Arrhenius law, increasing the temperature accelerates the rate of reaction [6]. However, in line with the Le Chatelier principle (thermodynamics), a temperature decrease shifts the equilibrium to the right [7]. Favorable thermodynamic conditions, promoting CO conversion and high hydrogen yield, result from exothermic reactions [8]. The shift conversion reaction in industry is operated in two stages, including at high and low temperature.

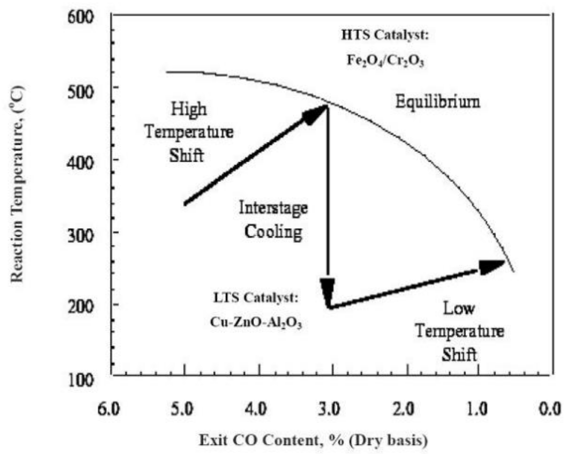

Figure 1. Water gas shift reaction scheme [9]

Figure 1 shows the relationship between the reaction temperature and the percentage of unreacted CO, where in the High-Temperature Shift Converter (HTSC) the percentage of unreacted CO is around 3%. Subsequently, CO conversion is relatively low when the operating temperature deviates significantly from the equilibrium temperature. Raising the temperature is required to improve conversion and quicken the rate of reaction. The concentration of CO decreases in the reactor due to the greater temperature, while the concentration of H_2 and CO_2 increases. CO_2 and H_2 concentrations will rise until the reactor achieves its maximum temperature, however, excessive temperature increases will lead the reduction in the composition of CO_2 and H_2. This happens as the reaction reaches equilibrium, shifting to the left and raising the CO concentration.[10].

CO in the process gas is undesirable due to its toxicity in catalyst of ammonia converter, necessitating purification from the process [11]. This includes shift conversion of CO to CO_2 followed by re-converted in the methanator. Shift conversion to CO occurs in HTSC and Low-Temperature Shift Converter (LTSC) within the ammonia plant. Inadequate catalyst performance in HTSC can diminish conversion rates and elevate the workload on LTSC. Catalyst in HTSC is replaced periodically during every Factory Turn Around to maintain the performance of HTSC device. Therefore, this research aimed to analyze the performance of catalyst life based on the percent CO conversion, temperature, and pressure drop parameters. The objective is to determine the most effective duration for using HTSC catalyst.

2. Research Methods

The analysis of catalyst lifetime in HTSC (104-D1) process unit at PUSRI II-B Factory involved several stages of data collection. This included obtaining essential data such as design and actual data from June 2021 to November 2022. The evaluation flowchart of HTSC (104-D1) at the PUSRI II-B Factory is shown in Figure 2.

2.1 Primary Data

Primary data, obtained directly from the field during the operation of HTSC unit with a non-isothermal system, was collected from PUSRI-IIB ammonia factory data (Department of Operations and PUSRI-IIB Ammonia Control Room log sheet). Table 1 shows the design data obtained from PT. Pupuk Sriwidjaja Palembang handbook, including data on the operating conditions of the tool at factory start-up (initial factory start conditions).

Table 1. HTSC (104-D1) design data

Parameter	Inlet	Outlet
Temperature (°C)	371	431
CO (kmol/hr)	1660,981	507,854
CO_2 (kmol/hr)	1230,981	2384,175

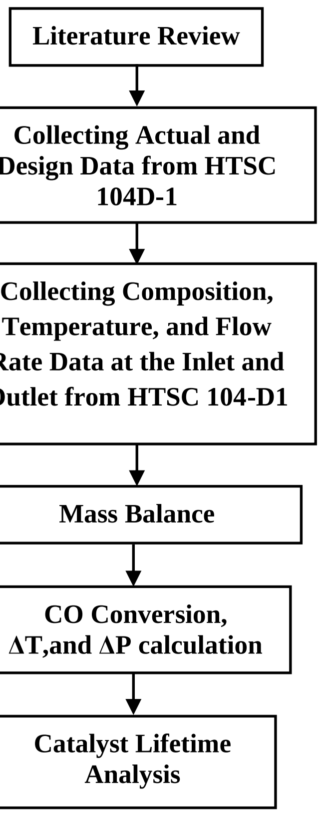

Figure 2. Flow diagram of catalyst lifetime analysis on HTSC (104-D1)

2.2 Secondary Data

Secondary data was obtained from several references such as handbook, journals, PUSRI website, and the philosophy of the production process. Calculation of CO to CO_2 conversion in HTSC (104-D1) follows Equation 1.

$$\% \, Conversion = \frac{Mol \, Outlet - Mol \, Inlet}{Mol \, Inlet} \times 100\% \quad \text{....(1)}$$

3. Results and Discussion

The reaction in HTSC is both reversible and exothermic, influenced by the elevated operating temperature observed at HTSC outlet. The performance of HTSC (104-D1) is affected by temperature, steam-to-gas ratio, pressure drop, and % CO in an outlet. An elevated steam-to-carbon (S/CO) ratio improves the conversion of CO_2 and H_2, resulting in a decrease in CO concentration. Under these conditions, the diminishing CO concentration shows a decline in equipment efficiency [10].

Catalyst used in a reaction, at a certain time, will have a decrease in activity, due to its age or lifetime. Catalyst life is defined as a period during which it produces the desired reaction product greater than the reaction product without a catalyst [12].

Water gas shift HTSC catalysts have been extensively examined and widely used industrially because of the low cost, long service life (3–5 years), and resistance to poisoning. They are usually operated in a temperature range of about 320–450 °C (non-isothermal system). Most HTSC catalysts are based on Fe_2O_3 (80–90 wt.%) and Cr_2O_3 (8–10 wt.%), with the balance being promoters/stabilizers (e.g. CuO_2, Al_2O_3, alkali, MgO, ZnO) [13].

Table 2. CO conversion, ΔT, and ΔP calculations of HTSC (104-D1)

No	Month	CO (kmol/h)		Conversion (%)	ΔT (^{O}C)	ΔP (kg/cm^2)
		Inlet	Outlet			
X	Design	1660.982	507.854	69.425	60.000	-
1	June 2021	1102.704	359.184	67.427	63.070	0.350
2	July 2021	1149.302	249.165	78.320	69.240	0.260
3	August 2021	1248.635	275.537	77.933	67.270	0.280
4	September 2021	1274.798	283.677	77.747	66.210	0.280
5	October 2021	1288.542	291.262	77.396	66.170	0.280
6	November 2021	1280.771	292.514	77.161	66.150	0.280
7	December 2021	1296.887	297.514	77.059	66.030	0.280
8	January 2022	1246.709	287.613	76.930	66.020	0.280
9	February 2022	1189.501	275.534	76.836	65.890	0.280
10	March 2022	1252.396	290.275	76.822	65.860	0.290
11	April 2022	1255.232	297.012	76.338	65.850	0.290
12	May 2022	1046.003	247.686	76.321	65.780	0.290
13	June 2022	1234.163	292.637	76.289	65.710	0.290
14	July 2022	1205.799	287.149	76.186	65.670	0.290
15	August 2022	1300.303	312.539	75.964	65.660	0.290
16	September 2022	1198.742	292.433	75.605	65.550	0.290
17	October 2022	1258.706	307.306	75.586	65.370	0.290
18	November 2022	1224.946	302.621	75.295	65.220	0.290

The Copper-Promoted Iron catalyst utilized in HTSC (104-D1) belongs to the Shift-Max 120 type, specifically designed for converting CO to CO_2 through the water shift reaction at operating conditions of 330–500°C. Catalyst chemical composition includes Fe_2O_3 89%, Cr_2O_3 8%, CuO 1.8%, and sulfur less than 150 ppm [14]. The physical properties of the Copper-Promoted Iron catalyst are in the form of domed tablets with a density of 1.08 kg/L, a volume of 65 m^3, a mass of 70,200 kg, and a size of 6 x 6 mm.

Data for calculating catalyst lifetime analysis comprises both the design data of HTSC (104-D1) and the actual operational data, shown in Table 2. Table 2 shows the data obtained from June 2021 to November 2022. Catalyst performance in HTSC (104D-1) was still far above the design data. The Copper-Promoted Iron catalyst was replaced during Turn Around in June 2021, and serves as reference data for conditions pre-replacement.

Based on the observed data, the performance of catalyst in HTSC (104D-1) has decreased step by step. Subsequently, the June 2021 data, representing conditions before Turn Around, shows a performance below the design specifications, signaling the need for catalyst replacement. There are several parameters observed to investigate catalyst performance and lifetime. The parameters used are pressure drop (ΔP), temperature profile (ΔT), and percent CO conversion on HTSC (104D-1) [15].

3.1 Catalyst performance according to pressure drop (ΔP)

Pressure drop is an operating condition that can be used to review catalyst performance because the value of the pressure drop is related to the reaction conversion that occurs. A higher pressure drop tends to decrease reaction conversion, leading to unreacted reactants [16].

The pressure drop graph in Figure 3 shows a linear trend, implying that over time, the pressure drop increases. June 2021 pressure drop data serves as a reference due to the absence of available design data. This particular dataset is selected as a reference because it represents the last operating condition before Turn-Around. Subsequently, from July 2021 - November 2022, the value of the pressure drop tends to increase periodically, approaching the pressure drop value of the reference data. This condition shows that catalyst performance has decreased, specifically on the active side. According to the research conducted by Utomo & Laksono [17], it was reported that one of the causes of catalyst deactivation, namely fouling, occurred due to material clumping on the active side. The increase in the amount of relatively large deposits will close the active sites of catalyst, and fouling of catalyst will increase the pressure drop in the reactor.

A decrease in catalyst activity may stem from obstructed pores, creating a pressure difference between the inlet and outlet. Closed catalyst pores may result from compounds that act as poisons. These chemical compounds cover catalyst pores as their molecular size exceeds that of pores [18]. The closed catalyst pores will prevent CO gas from reacting with H_2O to form CO_2, causing a decrease in CO conversion from the design level. CO that escapes will exacerbate the performance of the next shift conversion process unit, namely LTSC (104D-2A/B).

Based on the graph obtained, the trendline is 0.655. This showed that the data obtained has sufficient validity to be used as a review of catalyst performance evaluation. This means that 65.50% of the data is valid to show the performance of catalyst.

From the graph equation and using the goal-seek method, the remaining lifetime of catalyst can be predicted. By substituting the value 0.35 as y on the graph, the corresponding month shows when catalyst will reach a value of 0.35. From this data, the remaining lifetime is calculated as 3 years and 6 months. This implies that catalyst can continue to be used for the next 3.5 years, showing an actual catalyst lifetime of 4 years and 11 months since catalyst replacement.

According to the data, the lower process conditions affect lifetime of the use of catalyst. This is also supported by the condition of the pressure drop which is still below the reference. The use of catalysts for many years will result in the accumulation of these catalyst-toxic compounds increasing every year. Although the actual concentration is very small and negligible, it can lead to large accumulations over several years. The result is that catalyst will be deactivated [19].

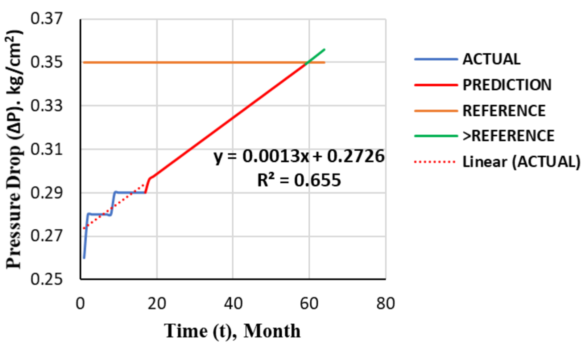

Figure 3. Effect of time on pressure drop

3.2 Catalyst performance according to temperature (ΔT)

Temperature is an integral factor in chemical reactions, particularly in industrial processes. It is closely tied to the minimum energy required to initiate a chemical reaction, known as activation energy [18]. The reaction in HTSC is exothermic. In an exothermic reaction, the enthalpy value of the reactants is greater than the enthalpy of the products, which results in the release of heat from the system to the surroundings. Therefore, the increase in temperature in HTSC shows that a reaction has occurred in the process equipment.

Achieving a high CO conversion percentage is possible with low operating temperatures, but it is crucial to maintain the temperature above the steam condensation point. An increase in the temperature profile causes the equilibrium to shift to the left, thereby CO exit is greater, but kinetically, the high temperature can accelerate the reaction rate and approach conversion at equilibrium conditions [20]. Elevated temperatures are problematic as they can harm the HTSC catalyst, leading to reduced performance. Maintaining an optimal temperature is crucial for the efficient conversion of CO to CO2, preventing issues such as catalyst deactivation through sintering. Sintering results in a decreased contact surface area, consequently diminishing catalyst activity [5].

Based on the graph in Figure 4, the actual data tends to form a linear line, the trendline of the graph obtained is 0.5498. This shows that the data obtained has sufficient validity to be used as a review of catalyst performance evaluation. This means that 54.98% of the data is valid to show the performance of catalyst. The actual data for July 2021 – and November 2022 appears quite distant from the design data which shows that HTSC catalyst is still functioning properly starting from catalyst replacement period until November 2022.

According to the graph equation and using the goal-seek method, the remaining catalyst lifetime can be predicted. Substituting a y-value of 60 into the graph predicts a remaining catalyst lifetime of 3 years. Consequently, catalyst is projected to be usable for the next 3 years, contributing to a total catalyst lifetime of 4 years and 5 months. This estimation guides considerations for catalyst replacement. The difference in lifetime is due to the small percentage of data validation. Despite their differences, they can be taken into account when considering catalyst replacement.

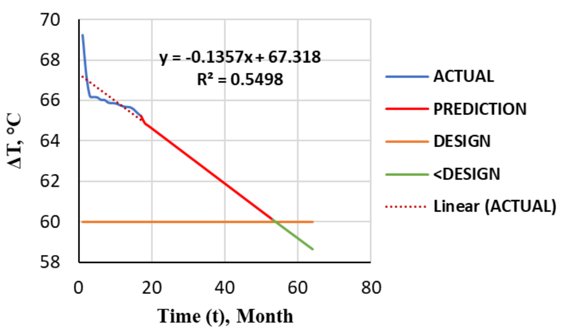

Figure 4. The effect of time on the temperature

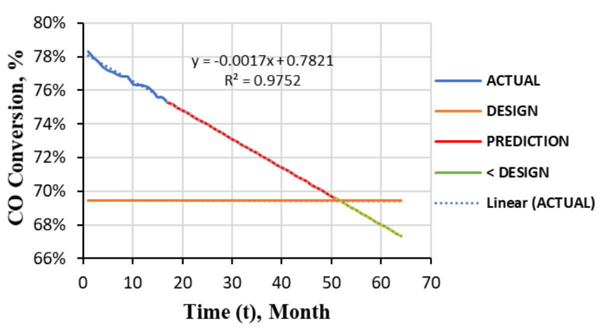

Figure 5. Effect of time on CO conversion

3.3 Catalyst performance according to CO conversion

Conversion shows the extent to which the reactants transform into products, serving as a crucial indicator for catalyst performance. Various operating conditions, including pressure drop, influence conversion. A higher pressure drop correlates with lower reaction conversion in the process [16]. Based on PT. Pupuk Sriwidjaja handbook, the shift converter targets around ±70% CO conversion in HTSC, with nearly perfect CO conversion in LTSC. The design data shows a conversion value of 69.42% which is quite appropriate. However, data for June 2021 shows a value of 67.43% which shows that the performance of catalyst is below the design data.

Based on the graph in Figure 5, the actual data tends to form a linear line, the trendline of the graph obtained is 0.9752. This shows that the data obtained has great validity to be used as a review of the catalyst performance evaluation. This means that 97.52% of the data is valid to show the performance of catalyst. Actual data for July 2021 - November 2022 appears quite distant from the design data, which shows that HTSC catalyst is still functioning properly starting from catalyst replacement period until November 2022.

From the graph equation and using the goal-seek method, the remaining lifetime of the catalyst can be predicted. Substituting a y-value of 69.42 into the graph predicts a remaining catalyst lifetime of 3 years. This projection shows that catalyst is expected to remain effective for the next 3 years, providing valuable information for ongoing usage and replacement considerations.

In June 2021, the Turn Around operation aimed to clean equipment and replace catalysts on the HTSC bed, to enhance production efficiency and increase CO conversion. Data for June 2021 showed a conversion value of about 67.43%, despite being below the designed value, this data remained valuable as a reference since it represents the latest information just before catalyst replacement. Substitute 67.43 for y on the graph to determine when the catalyst value reaches 67.43. With this information, the catalyst has a remaining lifetime of 3 years and 10 months, showing that it can be used for a total of 4 years and 8 months.

The data shows that the catch unit can still operate with a conversion percentage below the design data, although it is still about ±70%. The consequence of this is an increased workload for LTSC, the subsequent shift converter unit. The observed decrease in conversion suggests a potential decline in catalyst activity. Concurrently, a reduction in conversion implies a decrease in catalyst activity [21]. The actual conversion, however, is not only influenced by catalyst activity but also by factors such as pressure drop, amount of incoming feed, flow rate, etc. [22]. There is a direct relationship between catalyst activity and conversion. If catalyst activity decreases, it leads to a subsequent decrease in the reaction conversion in the shift converter [23].

4. Conclusion

In conclusion, this research showed that pores on the active side of the catalyst produce a greater pressure drop (ΔP), which lowers the CO conversion percentage and degrades catalyst performance. The increase in temperature (ΔT) in HTSC showed an exothermic reaction that occurred. The optimal reaction rate occurred at a high temperature, while the equilibrium occurred at a low temperature. CO conversion is directly proportional to HTSC catalyst performance, with decreased conversion signaling a decline in catalyst effectiveness. Catalyst on HTSC (104-D1) can be used for 4 years and 8 months after its replacement.

References

[1] Aziz, M., TriWijayanta, A., & Nandiyanto, A. B. D. (2020). Ammonia as effective hydrogen storage: A review on production, storage and utilization. *Energies*, 13(12), 3062. doi: 10.3390/en13123062

[2] PT Pupuk Sriwidjaja Palembang (Pusri). (2023). Anhydrous ammonia. *Ammonia Product*. Retrieved from https://www.pusri.co.id/en/product/ammonia/anhydrous-ammonia

[3] Felder, R. M., Rousseau, R. W. (2009). *Elementary Principles of Chemical Processes*. (L. Linda, Ed.)*John Wiley & Sons, Inc* (4th ed.). United States of America: Laurie Rosatone.

[4] PT Pupuk Sriwidjaja Palembang (Pusri). (2017). *Filosofi proses pabrik ammonia PUSRI – IIB kapasitas produksi 2000 MTPD* (2nd ed.). Palembang: PT. Pusri Palembang.

[5] Pal, D. B., Chand, R., Upadhyay, S. N., & Mishra, P. K. (2018). Performance of water gas shift reaction catalysts: A review. *Renewable and Sustainable Energy Reviews*, 93, 549–565. doi: 10.1016/j.rser.2018.05.003

[6] Kohout, J. (2021). Modified arrhenius equation in materials science, chemistry and biology. *Molecules*, 26(23), 1–19. doi: 10.3390/molecules26237162

[7] Ojelade, O. A., & Zaman, S. F. (2021). Ammonia decomposition for hydrogen production: a thermodynamic study. *Chemical Papers*, 75(1), 57–65. doi: 10.1007/s11696-020-01278-z

[8] Chen, W. H., & Chen, C. Y. (2020). Water gas shift reaction for hydrogen production and carbon dioxide capture: A review. *Applied Energy*, 258, 1–25. doi: 10.1016/j.apenergy.2019.114078

[9] Benny, S. (2010). *High Temperature Water Gas Shift Catalysts : A Computer Modelling Study*.

Johnson Matthey Technology Centre. University College London.

[10] Patra, T. K., Mukherjee, S., & Sheth, P. N. (2019). Process simulation of hydrogen rich gas production from producer gas using HTS catalysis. *Energy*, 173, 1130–1140. doi: 10.1016/j.energy.2019.02.136

[11] Zhang, Z., Wu, Z., Rincon, D., & Christofides, P. D. (2019). Operational safety of an ammonia process network via model predictive control. *Chemical Engineering Research and Design*, 146, 277–289. doi: 10.1016/j.cherd.2019.04.004

[12] Hughes, R. (1989). Activation, Deactivation and Poisoning of Catalysts. *Chemical Engineering Science*, 44(8), 1747–1748. doi: 10.1016/0009-2509(89)80018-1

[13] Shekhawat, D., Spivey, J. J., & Berry, D. A. (2011). *Fuel Cells: Technologies for Fuel Processing*. *Fuel Cells: Technologies for Fuel Processing*. Amsterdam: Elsevier Science. doi: 10.1016/C2009-0-20328-X

[14] Baboo, P. (2015). Catalyst in Amonia Plant and Their PerformanceEvaluation. National fertilizers Ltd, India.

[15] Wahdaniyah, N. (2018). *Evaluasi Kinerja Katalis Methanator (106-D) Unit Amonia Operasi Pabrik-2 Pt. Pupuk Kalimantan Timur-Bontang*. Politeknik Ati Makassar.

[16] Schmidt, L. D. (2005). *Engineering of Chemical Reactions*. *Engineering of Chemical Reactions* (2nd ed.). New York: Oxford University Press.

[17] Utomo, M. P., & Laksono, E. W. (2007). Tinjauan umum tentang deaktivasi katalis pada reaksi katalisis heterogen. In *Prosiding Seminar Nasional Penelitian, Pendidikan, dan Penerapan MIPA* (pp. 110–115). Yogyakarta: Universitas Negeri Yogyakarta.

[18] Suarsa, I. W. (2017). Teori Tumbukan Pada Laju Reaksi Kimia. *Pengembangan Bahan Ajar*. Denpasar: Jurusan Teknik Kimia, FMIPA, Universitas Udayana.

[19] Dunleavy, J. K. (2006). Sulfur as a catalyst poison. *Platinum Metals Review*, 50(2), 110. doi: 10.1595/147106706X111456

[20] Uningtya, N. (2018). *Evaluasi kinerja katalis pada high temperature shift converter dan low temperature shift converter (104-D) di unit amonia PUSRI-IV*. Univesitas Pembangunan Nasional “Veteran” Yogyakarta.

[21] Baraj, E., Ciahotný, K., & Hlinčík, T. (2022). Advanced Catalysts for the Water Gas Shift Reaction. *Crystals*, 12(4), 509. doi: 10.3390/cryst12040509

[22] Dey, S., & Mehta, N. S. (2022). Low temperature catalytic conversion of carbon monoxide by the application of novel perovskite catalysts. *Science in One Health*, 1. doi: 10.1016/j.soh.2022.100002

[23] Farah, E., Demianenko, L., Engvall, K., & Kantarelis, E. (2023). Controlling the Activity and Selectivity of HZSM-5 Catalysts in the Conversion of Biomass-Derived Oxygenates Using Hierarchical Structures: The Effect of Crystalline Size and Intracrystalline Pore Dimensions on Olefins Selectivity and Catalyst Deactivatio. *Topics in Catalysis*, 66, 1310–1328. doi: 10.1007/s11244-023-01833-4