Dynamic operation of water gas shift reaction over Fe₂O₃/Cr₂O₃/CuO catalyst in Pd/Al₂O₃ membrane reactor

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Abstract. Hydrogen has been considered as promising energy carrier that can be produced from renewable resources, such as biomass through gasification. This process results in producer gas containing CO, CO₂, H₂, N₂, and CH₄. The conventional enhancement of hydrogen is typically conducted using several unit operations such as water gas shift reactor (WGSR) and separation unit such as Pressure Swing Adsorption (PSA). Process intensification offers a new method to integrate both WGSR and separation unit into single membrane reactor. This research aimed to investigate the influence of dynamic operation on membrane reactor performance. The steady state fixed bed reactor and membrane reactor were used as base case to judge the performance of dynamic membrane reactor. The water gas shift reaction over Fe₂O₃/Cr₂O₃/CuO was carried out at 350°C and 1 atm by varying the feed composition and gas residence time. The feed composition ratio of H₂O/CO consisted of 2 and 3 on mole basis, while the gas residence times were 1.2 s and 2.3 s. The membrane reactor consists of shell and tube sides made of Pd/Al₂O₃ material with technical specification of 10 mm inner diameter, 20 μm Pd thickness supported by alumina, and 10 cm reactor length. The compositions of the feed gas and products were measured using gas analysers such CO gas detector (Bacharach PCA® 3) and H₂ gas detector (Cosmos XP-3140). The dynamic operation was performed following the square wave perturbation of the feed gas at switching time of 15 s. The experiment results showed that increasing the feed composition ratio and gas residence time increased the conversion of CO and hydrogen production in the fixed bed reactor and membrane reactor. Higher production of hydrogen also improved the recovery of hydrogen in membrane reactor. The use of membrane reactor increased significantly the conversion of CO when compared to fixed bed reactor. Moreover, the dynamic membrane reactor would give much better performance in term of CO conversion and hydrogen recovery. The stability of the Pd/Al₂O₃ membrane reactor was proven for at least 10 h operation.

1. Introduction
Nowadays, many researchers develop sustainable energy resources due to limitation to fossil fuel. Hydrogen is expected and has been widely agreed as an alternative energy instead of fossil fuels because it is clean, environmentally friendly, and can be produced from various resources [1]. The energy density of hydrogen per mass unit is approximately 2.6 times higher than LPG [2]. Hydrogen could also be easily converted to electricity by fuel cell technology [3].
Water Gas Shift Reaction (WGSR) is often used as synthesis path to enhance the production of hydrogen. The WGSR typically converts carbon monoxide (CO) by using steam to produce hydrogen and CO₂. The WGSR is an exothermic and reversible reaction, and therefore it is highly influenced by operating conditions. The enhancement of H₂O/CO ratio will increase the CO conversion [4] and prevent the carbon deposition in catalyst [5]. High reaction temperature will increase the reaction rate, while low temperature will increase the conversion. As consequence, the optimum design of WGSR results in two reactors in series, which are High Temperature Shift Converter (HTSC) and the Low Temperature Shift Converter (LTSC). High purity hydrogen can only be obtained through product separation process.

Process intensification opens new way in integrating the HTSC and LTSC, results in the so-called palladium (Pd) membrane reactor. Stankiewicz and Moulijn [6,7] defined process intensification as the development of novel equipment, processing techniques, and methods, when compared to traditional ones, offer substantial improvements in (bio) chemical processes. This technique will make the process more economical and efficient. Pd is a metal that have high permeability and selectivity of hydrogen [8]. Hydrogen diffused through Pd membrane according to solution-diffusion mechanism [9]. Enhancement of mechanical strength and reduction of capital expenditure can be achieved by setting a membrane support, such as alumina (Al₂O₃). The catalyst used in membrane reactor for WGSR is normal catalyst such as iron oxide.

There are many variables that influence the membrane performance, such as pressure difference, reaction temperature, sweep gas velocity, palladium thickness, and H₂O/CO feed ratio [10,11]. The membrane permeability during steady state operation could decrease over time due to concentration polarization and inhibition [12]. Low hydrogen recovery during steady state operation can also be induced by surface deactivation. The dynamic operation can produce higher hydrogen recovery through when certain time scale is applied. A square wave perturbation can be created by modulating the feed flow rate in high and low value at certain switching time [13,14]. According to Hoebink et al. [15], there are three different regimes of unsteady state operation: relaxed steady state (sliding), dynamic, and quasy-steady state.

2. Materials and Methods

2.1. Experimental System

Materials used in this research consist of high purity gases (H₂, N₂, CO), steam, Fe₃O₃/Cr₂O₃/CuO catalyst (90/8/2.5 wt%), density 1.12 kg/L, and surface area is about 110 m²/g) in the range of 60 mesh to 80 mesh, inert for catalyst dilution in the fixed bed reactor, and liquid soap as the carrier of gas volumetric flow measurement. The fixed bed reactor has length (L) of 34.5 cm and inside diameter (ID) of 10 mm. The catalyst bed length inside the reactor is 5 cm. Meanwhile, the membrane reactor (L = 10 cm and ID = 10 mm) consists of Pd and porous Al₂O₃ layer with a thickness of 20 μm and 2 mm, respectively. The catalyst is placed on the shell side of membrane reactor. Feed and sweep gas (N₂, 5 ml/s) are flowed on a co-current configuration. Water was introduced to the reactor inlet through syringe pump then heated by heating coil. The heat needed for reaction was supplied by tube furnace. The reaction products were analysed by CO gas detector (Bacharach PCA® 3) and H₂ gas detector (Cosmos XP-3140). Both main equipment schemes are presented in Figure 1. Steady state operation in membrane reactor was carried out without modulator.

2.2. Experimental Procedure

The catalytic WGSR was conducted in the fixed bed reactor and Pd/Al₂O₃ membrane reactor. Based on Augustine [11], purging the reactor was accomplished by flowing N₂ for 30 minutes. The catalyst was subsequently activated by flowing steam and H₂ (1:1) for an hour at 400°C, followed by second purging using N₂ for 15 minutes and decreasing the temperature to reaction temperature of 350°C. After purging, heating, and activating the catalyst, main experiments were performed according to the specified variations. Data interpretations consist of CO conversion (Xₐₐ) and hydrogen recovery (HR).
3. Results and Discussion

3.1. WGSR using Fixed Bed Reactor

The conversion of CO at space time of 1.2 s (GHSV 3,130 h⁻¹) achieved 7.5% and 11.5% for H₂O/CO ratio 2 and 3, respectively. Meanwhile, CO conversion is 9.8% and 13.2% for H₂O/CO ratio 2 and 3 at 2.3 s space time. The CO conversion results for all variations are presented in Figure 2. Based on work from Demirel and Azcan [16], enhancement of steam in feed will shift the reaction equilibrium to the product so it increases the production of H₂. As the result, it increases CO conversion. Meanwhile, the higher the space time inside the reactor, the longer time for the reaction to be occurred. Longer reaction time increases the amount of reactants to produce H₂ as the main product. Therefore, experiments with higher space time resulted in higher CO conversion. Fishtik and Datta [17] found the same tendencies.

![Figure 2. CO conversion in fixed bed reactor with H₂O/CO ratio = 2 (○) and H₂O/CO ratio = 3 (●)](image)

3.2. Performance of Membrane Reactor in Steady State Operation

The performance of membrane reactor indicated in CO conversion and H₂ recovery was investigated at 350°C by varying feed composition and space time. The experiment results are presented in Figure 3. At the same space time (2.3 s), when the feed ratio (H₂O/CO) was 2, the CO conversion reached 47.4% and H₂ recovery was 40.4%. Meanwhile, when feed ratio was 3, the CO conversion reached 55.4% and H₂ recovery was 59.8%. Increasing the steam flow rate will shift the reaction equilibrium toward the product due to thermodynamic aspect. As the result, CO conversion is high. Moreover, hydrogen produced by WGSR in membrane reactor was continuously permeating to the tube side, leading to increased H₂ production significantly. This result showed the same tendency as research conducted by Uemiya et al. [10] and Augustine et al. [11].
Figure 3. CO conversion (●) and H$_2$ recovery (◌) as function of H$_2$O/CO feed ratio in space time=2.3s

The experiment was also conducted out for space time of 1.2 s (GHSV 3130 h$^{-1}$) and 2.3 s (1585 h$^{-1}$) to evaluate the effect of space time in the membrane reactor. The feed ratio in this experiment remained constant at 3. The experiment results are shown in Figure 4. When the space time is 1.2 s, CO conversion is 50.5%. Meanwhile, H$_2$ recovery reached 46.4%. Experiment which is held in space time 2.3 s shows higher CO conversion and H$_2$ recovery. CO conversion and H$_2$ recovery value respectively are 55.4% and 59.8%. The higher space time, the higher CO conversion and H$_2$ recovery. It is caused by longer time for reaction to be occurred in space time of 2.3s. As the result, variation in high space time produce high amount of H$_2$ and those H$_2$ have a proper chance to permeate through the membrane. Augustine et.al.[11] found the same tendencies.

Figure 4. CO conversion (●) and H$_2$ recovery (◌) as feed space time function in feed ratio of 3

3.3. Performance Comparison between Fixed Bed Reactor and Membrane Reactor

Referred to Le Chatelier principle, the equilibrium shifts to the reaction product if the product concentration decreases. The membrane reactor concept may improve H$_2$ recovery in the WGSR due to hydrogen separation through the membrane. In this work, the WGSR at 1 bar and 350°C showed better performance when using Pd/Al$_2$O$_3$ membrane reactor than fixed bed reactor. The comparisons of both results are shown in Figure 5. The conversion of CO at constant space time of 2.3 s achieved 9.8% and 13.2% for H$_2$O/CO ratio 2 and 3, respectively, at the experiment conducted in fixed bed reactor. Meanwhile, CO conversion is 47.4% and 55.4% for H$_2$O/CO ratio 2 and 3 at the experiment conducted in membrane reactor. This means that the use of Pd/Al$_2$O$_3$ membrane reactor gave much better performance than the use of conventional fixed bed reactor. The data is also supported by experiments with constant feed ratio=3.
3.4. Dynamic Operation in Membrane Reactor

Unsteady state operation or dynamic operation has been recognized as one of successful methods on process intensification to reach better performance. In this study, the dynamic operation was operated by applying a square wave disturbance periodically. The CO molar flow was periodically changed to disturb the membrane reactor, particularly the concentration fluctuation on the membrane surface. This dynamic concentration of CO on the surface of membrane at proper switching time would influence the solution diffusion rate. This dynamic WGSR experiment using Pd/Al2O3 membrane reactor was operated at 1 atm and 350°C with H2O/CO ratio of 2, space time 2.3 s and the switching time was 15 s. Figure 6 shows the dynamic CO conversion and Hydrogen recovery as function of time on stream after stable oscillation. Based on Hoebink et al. [15], the regime of operation formed in this switching time was dynamic, indicating that the system may respond the dynamic perturbation.

Figure 5. CO conversion as function of H2O/CO ratio in space time=2.3s (left) and of space time in feed ratio=3 (right) in Pd/Al2O3 membrane reactor (●) and fixed bed reactor (○)

Figure 6. CO conversion (●) and H2 recovery (○) in dynamic operation of membrane reactor

Figure 7. Comparison of CO conversion (●) and H2 recovery (○) between steady state and dynamic operation of WGSR using Pd/Al2O3 membrane reactor
The comparison of membrane reactor performance under steady state and dynamic operation is presented in figure 7. The CO conversion and H₂ recovery resulted from steady state operation were 47.6 % and 40.3%, respectively. Meanwhile, the CO conversion and H₂ recovery resulted from dynamic operation exceeded 58.0% and 41.5%, respectively. The dynamic operation increased the CO conversion and H₂ recovery because it was able to create “sweeping” effect by changing the feed flow rate that minimized the concentration polarization effect (external mass transfer resistance) over the membrane surface.

4. Conclusion
The WGSR to produce hydrogen has been studied in the fixed bed reactor and membrane reactor either under steady state and dynamic operation. In both fixed bed and membrane reactor, increasing H₂O/CO ratio and space time gave rise to the increased CO conversion. In WGSR using Pd/Al₂O₃ membrane reactor over iron oxide catalyst, increasing of H₂O/CO ratio and space time also increased H₂ recovery. The performance of Pd/Al₂O₃ membrane reactor for WGSR has proven to be better than fixed bed reactor for various operation conditions in term of CO conversion and H₂ recovery. The dynamic operation in the membrane reactor improves higher CO conversion and H₂ recovery compared with steady state operation.

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6. References
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