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# Reduction in CO emissions along a two-stage hydrogen-permselective membrane reactor in methanol synthesis process

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ABSTRACT

Carbon monoxide (CO) is a scentless and invisible gas that is quite poisonous. It is also known to be a major environmental pollutant. Industrial chemical processes contribute to CO pollution levels in the atmosphere. One of the most important processes for controlling the carbon monoxide content is conversion of CO to methanol by catalytic hydrogenation. The present work investigates enhancement of CO conversion in a conventional two-stage methanol synthesis reactor using a hydrogen-permselective membrane. For this membrane system, a one-dimensional dynamic plug flow model was proposed in the presence of long-term catalyst deactivation. This model compares CO removal in a membrane two-stage methanol synthesis reactor with a conventional two-stage methanol synthesis reactor. A conventional two-stage reactor is a vertical shell and tube in which the first reactor coolant is saturated water and the second one is cooled with synthesis gas. In a membrane two-stage reactor, the wall of the tubes in the gas-cooled reactor is coated with a Pd–Ag membrane, which only permits the diffusion of hydrogen. For validation of the recommended dynamic model, the measured daily process data of a methanol plant recorded for a period of 4 years were used and a good agreement was obtained.
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## 1. Introduction

Carbon monoxide (CO) is a colorless, odorless and toxic gas that even at low levels of exposure is very dangerous for human health and environment. CO can starve critical body organs, especially the brain and heart, of oxygen. Once inside the lungs, CO molecules pass easily into the bloodstream and compete with oxygen for hemoglobin in the red blood cells. In addition, the industrial applications of environmental technology have increased and reduction in CO concentration can significantly counteract the growth of $CH_4$ in the atmosphere, so it has important indirect effects on global warming [1,2]. To minimize these effects, the carbon monoxide emissions from industrial sources have to be decreased. One possible approach is recycling and fixing CO in a chemical process to form useful products such as methanol which is regarded as the effective method to reduce carbon monoxide concentration in the atmosphere. Methanol is widely used as a feedstock for the production of chemicals and is considered as a viable source for the generation of hydrogen for fuel cell application. It is a suitable fuel to produce hydrogen by steam reforming because of low operating temperatures (250–300 °C), low expense, simple to storage and eminent miscibility with water. Hydrogen plays a major role in the future as a carbon-free fuel for installing $H_2$ reforming unit to a portable fuel cell, compact design of reformer is mainly the strategic point [3–6]. Commercially, methanol can be recovered from many resources and is produced by catalytic conversion of synthesis gas in large scale. Synthesis gas consists of CO, $CO_2$, and $H_2$ and some inert components like $CH_4$ and $N_2$.

At the entrance of the methanol reactor, the reactions are rate base, so increasing temperature enhances rate of reaction and CO conversion, but at the end of reactor, the reactions are equilibrium base and increasing temperature, decreases CO equilibrium conversion. Therefore, in order to reach the highest removal rate of CO, implementing a higher temperature at the entrance of the reactor and then reducing temperature gradually towards the exit of reactor is one of the significant issues in methanol synthesis reactor.

Recently, a two-stage methanol synthesis reactor was introduced by Lurgi instead of a single-type for CO conversion to methanol [7]. This system is an advanced technology for converting synthesis gas to methanol at low cost and in large quantities. The configuration of this system is based on the two-stage reactor system. The first is a high temperature water-cooled reactor that is combined in series with a low temperature gas-cooled reactor and partial conversion of CO to methanol is

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accomplished in this reactor. Reacting gas composition in the second reactor is essentially poor in $H_2$, so performance of this reactor is lower than first reactor and decreases system efficiency. One way to reach higher conversion of CO to methanol is the addition of hydrogen to the reacting gas selectively by using membrane in gas-cooled reactor that leads to a shift of the chemical equilibrium towards the product side [8].

A membrane two-stage methanol synthesis reactor is a modified system which combines the chemical and membrane conversion in one system [9]. The main advantages of this system are: enhancement of CO conversion, overcoming with the potential limitations imposed by thermodynamic equilibrium [8], improvement of kinetics-limited reactions in the first reactor due to the higher feed temperature, enhancement of equilibrium limited reactions due to a lower temperature in the gas-cooled reactor and control of stoichiometric number of reacting gases along the second reactor by hydrogen diffusion through the membrane. The membrane separation is governed by both the chemical nature of the membrane material and the physical structure of the membrane [10]. Membrane conversion technology in chemical reaction processes is mainly used in reaction systems containing hydrogen and oxygen, and is based on inorganic membranes [11]. It was observed that diffusion of hydrogen through palladium membranes can enhance the selectivity of hydrogenation [12]. The use of Pd membranes is hindered because palladium shows a transition from the α-phase (hydrogen poor) to the β-phase (hydrogen rich) at temperatures below 300 °C and pressures below 2 MPa, depending on the hydrogen concentration in the metal. Since the lattice constant of the α-phase is 3% smaller than that of the β-phase this transition leads to lattice strain, and consequently after a few cycles, to a deformity of the metal lattice [13]. In many hydrogen-related reaction systems, Pd-alloy membranes on a stainless steel support were used as the hydrogen-permeable membrane [14]. A maximum value of hydrogen permeability is reached for an alloy with composition of 23 wt% silver [15].

For decades, palladium-based membranes have been used in transport of hydrogen because of their high permeability, good surface properties and 100% hydrogen selectivity [16]. These membranes combine hydrogen transition with distinguishing properties such as resistance to high temperatures, solvents, and corrosion. The main cause of the Pd-based membranes development is: low costs as well as perm-selectivity combined with good mechanical, thermal and long-term stability [17]. These properties make interesting use of palladium-based membranes such as Pd–Ag membranes in petrochemical industry.

There is one study on conversion of CO to methanol in Pd–Ag membrane single-type methanol synthesis reactor [8], but no investigation regarding the use of a Pd-membrane in two-stage methanol synthesis reactor for enhancement of CO conversion. Therefore, it was decided to first study on this system.

The aim of present work is reduction of carbon monoxide emission in a conventional two-stage methanol synthesis reactor. In this system, the walls of tubes in the gas-cooled reactor are covered with a layer of hydrogen perm-selective membrane. The driving force for hydrogen diffusion is its partial pressure gradient from feed synthesis gas to the reacting gas. The advantages of this concept will be discussed based on temperature, activity of catalyst and concentration profiles. The results are compared with the performance of conventional two-stage methanol synthesis reactor.

## 2. Process description

### 2.1. Conventional two-stage methanol synthesis reactor

Schematic diagram of a conventional two-stage methanol synthesis reactor is shown in Fig. 1.

The catalyst is packed in shell side of water-cooled reactor and vertical tubes of gas-cooled reactor. Reactions of methanol synthesis are performed over commercial $CuO/ZnO/Al_2O_3$ catalyst. Cold feed synthesis gas is fed to tubes of the second reactor and is flowing in counter-current mode with methanol-containing reacting gas in the shell of this reactor. Then outlet synthesis gas is entered to tubes of the first reactor and chemical reaction initiated by catalyst. The remaining heat of reaction is transferred to the cooling water inside the shell. In this stage, CO is partly converted to methanol. Then reacting gas mixture is left directing to the catalyst shell side of second reactor and its temperature is continuously reduced through the catalyst bed. Finally, the product is removed from the side stream of second reactor.

Temperature of the first reactor is higher than second reactor so the main catalyst deactivation occurs in this reactor. Therefore, the lower operating temperature in the gas-cooled reactor results in a practically unlimited catalyst service life. In addition, reaction control extends catalyst life time of the water-cooled reactor.

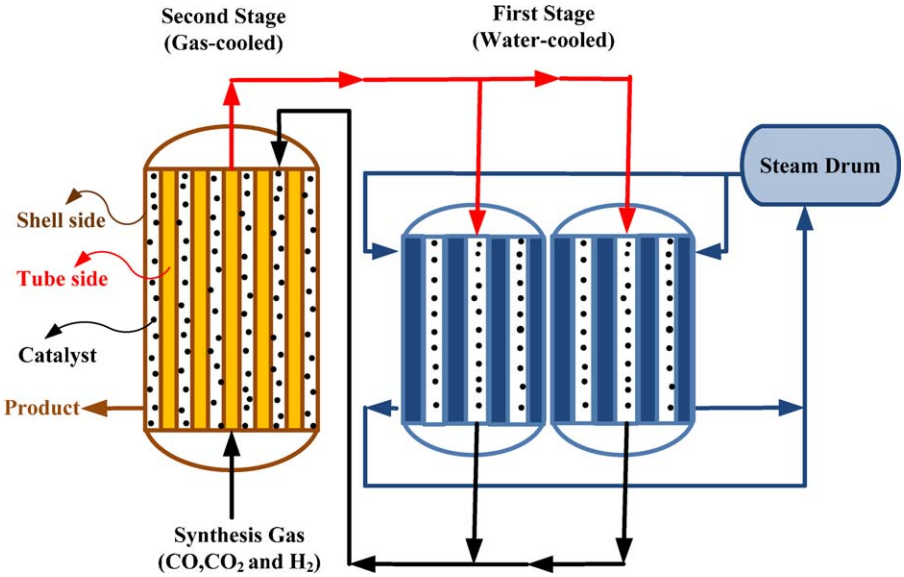


**Fig. 1.** Schematic flow diagram of conventional two-stage methanol synthesis reactor.

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