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# Enhancement of Gasoline Production in a Novel Optimized Hydrogen-Permselective Membrane Fischer-Tropsch Reactor in GTL Technology

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In this work, a novel hydrogen-permselective membrane Fischer-Tropsch reactor (MR) has been optimized using genetic algorithm (GA). In this configuration, the synthesis gas is fed to the tube side and flows in co-current mode with reacting gas mixture that enters in the shell side of the reactor. In this way, the synthesis gas is heated by heat of reaction which is produced in the reaction side. Hydrogen can penetrate from the feed synthesis gas side into the reaction side as a result of a hydrogen partial pressure difference. The outlet synthesis gas from tube side is recycled to shells and the chemical reaction is initiated in catalytic bed. Therefore, the reacting gas in shell side is cooled simultaneously with passing gas in tube and saturated water in outer shell. A theoretical investigation was performed in order to optimize the reactor performance, maximizing $C_5^+$ production and at the same time, minimizing the $CO_2$ yields as an undesired product. The optimization was carried out and the results show there is a favorable profile of FTS products along the optimized OMR system relative to the MR. Optimal catalyst size and temperature profile along the reactor were obtained and 3.1815 % additional $C_5^+$ yield was resulted in optimized system relative to membrane FTS reactor.

## 1. Introduction

Recently, the high oil price has created considerable interest in the development of alternative technology for the manufacture of transportation fuels. The gas-to-liquid (GTL) process can be a good candidate for alleviating the current oil crisis, in which synthetic liquid fuels (e.g., gasoline, diesel, and wax) are produced from stranded natural gas. This means that 'stranded natural gas' in remote areas can be converted to shippable liquid fuels through the GTL process (Schulz, 1999 and Hall, 2005). In the GTL process, Fischer-Tropsch synthesis (FTS) is the key technology for converting synthesis gas (mixture of CO and $H_2$) to liquid fuels. The development of an effective catalyst and reactor system is the most competitive issue in FTS. Owing to the high demand on gasoline in the world and its higher price relative to that of diesel, production of gasoline from the FT process, becomes more favourable. The octane

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number of FT gasoline is lower than that of the gasoline obtained from crude oil processing, since the FT gasoline mainly consists of n-paraffin. To promote the yield and quality of the gasoline from Fischer-Tropsch synthesis, bifunctional catalysts have received extensive attention in the recent years (Cagnoli et al. 2002). A single stage fixed-bed FTS was developed in the Research Institute of Petroleum Industry (RIPI) to produce high octane, low sulfur gasoline by a modified bifuncthional Fe-HZSM5 catalyst. Such a process removes the need for a cumbersome upgrading unit for GTL plants (Forghani et al. 2009). Ahmadi Marvast et al. (2005) simulated the stated single stage fixed-bed FTS reactor (Marvast et al. 2005). The simulation results have showed a dispensable change in temperature and concentration profiles over 7m reactor length. Likewise, it has been observed that the reacting gas is $H_2$-poor in the second half of reactor and hydrogen adding into the system is necessary. "$H_2$-poor" means that the $H_2$/CO ratio is lower than the optimum ratio what is required for gasoline production. The presence of a permselective membrane in a reacting system showed that hydrogen feeding through palladium membranes can ameliorate the selectivity of hydrogenation (Roa et al. 2002). In this work, we aim to maximize the production of high octane gasoline on bifunctional Fe-HZSM5 catalyst through HTFT process in the membrane reactor. So, initially, this proposed concept is mathematically modelled and pursuant to simulation, an optimization approach is applied to determine the optimum of catalyst size, the optimal cooling water and feed gas temperature. Optimization tasks are investigated by novel optimization tools, genetic algorithms. Genetic algorithms (GAs) are imitation of natural evolution and are believed as powerful optimization techniques among stochastic methods. Consequently, maximum production rate of gasoline in proportion to utmost conversion of $CO_2$ to FTS products is obtained.

## 2. Process Description

### 2.1. Fixed-bed Single Stage FT Reactor (CR)

In conventional fixed bed Fischer-Tropsch reactors, multitubular reactors cooled by pressurized boiling water are often used. A FT synthesis pilot plant was designed and constructed by the RIPI and National Iranian Oil Company (RIPI-NIOC) in 2004 (Forghani et al. 2009).

### 2.2. Membrane Fischer-Tropsch reactor

Fig. 1 shows the schematic diagram of a membrane Fischer-Tropsch reactor in co-current configuration. This system consists of two concentric pipes like tube-shell system. The tube wall in this system is hydrogen-permselective and hydrogen partial pressure gradient between the shell and tube permits diffusion of hydrogen through the Pd based membrane layer. Therefore, the mass and heat transfer processes simultaneously occur between both sides resulting in higher heat transfer and controlling of $H_2$/CO ratio. This simulation study is based on a Pd–Ag layer thickness of 15 μm. In this configuration, the fresh synthesis gas is fed to the tube side (permeation side) and is preheated by the generated heat in reaction side (shell side). Pure hydrogen permeates to reaction side in order to control and maintain the suitable hydrogen gradient in the whole length of the reactor. Then, the heated synthesis gas is routed from

recycle stream through shell in a co-current mode with feed synthesis gas and the chemical reaction is initiated by the catalyst. The reacting gas is also cooled with cooling saturated water which flows around it. In fact, the heat of reaction is transferred to both cooling water and fresh synthesis gas. After leaving the shell, the product containing hydrocarbons goes to hydro cracking unit. Catalyst characteristics and specifications of membrane F-T reactor are the same as CR.

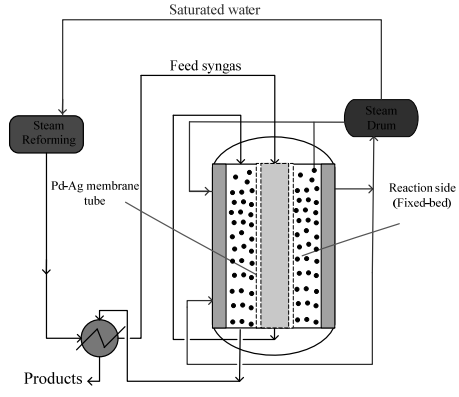


*Figure 1: Schematic diagram of a membrane Fischer-Tropsch reactor*

## 3. Mathematical model

A one-dimensional heterogeneous model comprising a set of heat and mass transfer equations and the kinetics of the main reactions are chosen in this work to simulate the combination of fixed and fluidized-bed membrane reactors.

### 3.1 Reaction network

The Fischer-Tropsch components include $H_2$, CO, $CO_2$, $H_2O$, $CH_4$, $C_2H_4$, $C_2H_6$, $C_3H_8$, n-$C_4H_{10}$, i-$C_4H_{10}$ and $C_5^+$. The following reactions are considered as dominate FTS reactions (Forghani et al. 2009).The reaction rate equation is as follows and the kinetic parameters are given in Table 3:

$$R_i = 0.278\ k_i \exp\left(\frac{-E_i}{RT}\right) P_{CO}^{m} . P_{H_2}^{n} \quad (1)$$

The used kinetic model is valid for temperature range of 290-310 °C; pressure rang of 15-23 bars and $H_2$/CO ratio range of 0.76-1.82 Kinetic parameter data is extracted in literature (Forghani et al. 2009).

#### 3.2.1 Membrane reactor (MR) model

*3.2.1.1 Shell side (Reaction side)*

The mass and energy balance for solid are the same as conventional reactor (CR).

Fluid phase:

$$-\frac{1}{A_c}\frac{\partial F_i^{sh}}{\partial z}+a_v c_t k_{gi}(y_{is}-y_i)+\frac{\alpha_H}{A_s}(\sqrt{P_H{}^t}-\sqrt{P_H{}^{sh}})=0 \qquad i=1,2,...,N-1 \tag{2}$$

$$-\frac{1}{A_{shell}}C_{pg}\frac{\partial(F^{sh}T)}{\partial z}+a_v h_f(T_s-T)+\frac{\alpha_H}{A_s}(\sqrt{P_H{}^t}-\sqrt{P_H{}^{sh}})c_{ph}(T_{tube}-T)+\frac{\pi D_i}{A_{shell}}U_{tube}(T_{tube}-T)+\frac{\pi D_o}{A_{shell}}U_{shell}(T_{shell}-T)=0 \tag{3}$$

*3.2.1.2. Tube side (Permeation side)*

The mass and energy balance equation for fluid phase are given:

$$-\frac{1}{A_c}\frac{\partial F_i^{t}}{\partial z}-\frac{\alpha_H}{A_c}(\sqrt{P_H{}^t}-\sqrt{P_H{}^{sh}})=0 \qquad i=1,2,...,N-1 \tag{4}$$

$$-\frac{1}{A_c}C_{pg}\frac{\partial(F^t T)}{\partial z}+\frac{\alpha_H}{A_s}(\sqrt{P_H{}^t}-\sqrt{P_H{}^{sh}})C_{ph}(T-T_{tube})+\frac{\pi D_i}{A_c}U_{tube}(T-T_{tube})=0 \tag{5}$$

## 4. Hydrogen permeation

The flux of hydrogen permeating through the palladium membrane, $j_H$, will depends on the difference in the hydrogen partial pressure on the two sides of the membrane. Here, the hydrogen permeation is determined assuming Sieverts' law (Forghani et al. 2009). When $\alpha_H$ is zero, the membrane is not permeable to hydrogen and the model is used for the conventional methanol reactor.

## 5. Optimization

Genetic algorithm is applied to determine the optimal reactor operating conditions for MR concept. Genetic algorithms are mathematical optimization methods that simulate a natural evolution process. The goal of this work is to maximize the gasoline production and minimize the $CO_2$ yield during operation period.

The constraint is the temperature of catalyst beds which should be less than 620 K (catalyst hot spot) along the reactor because at the temperatures higher than 620 K the catalyst will be deactivated. This constraint is stated with penalty function and equals "weight (hot spot temperature – catalyst temperature)" in order to obtain the reasonable solution. Thus, optimization problem is formulated as below:

$$Maxf = \frac{C_5^+ \quad yield}{CO_2 \quad yield}+10\,(620-T_s) \tag{7}$$

*Path constraint:* $T_s < 620$ (K)

The results of the optimization are summarized in Table 1.

*Table 1. The optimized parameters for first approach*

| $T_{shell}$ (K) | $T_F$ (K) | Particle size(m) |
|---|---|---|
| 550.0792 | 552.5302 | 0.0035 |

The simulation of membrane reactor is carried out using optimization results in Table 1 and the results of this simulation are shown in several figures. Fig. 2 present the yield profiles of FTS products along the MR and OMR According to Fig. 4(a), the gasoline yield obtained by the optimized membrane system is higher than MR. Also, this figure confirms the 3.1815 % additional yield of gasoline in OMR respect to MR. Clearly, seen the membrane system suppresses the formation of the undesired product, $CO_2$ and $CH_4$, and thus enhances the formation of the desired product, $C_5^+$. But, OMR system presents a lower $CO_2$ production than MR. Adding $H_2$ is possible to increase the conversion of $H_2O$ to $CO_2$ by WGS reaction, in OMR concept and on the other hand, leads to decrease of methane production. For exothermic systems such as Fischer-Tropsch synthesis achieve to lower temperature profiles is favourable.

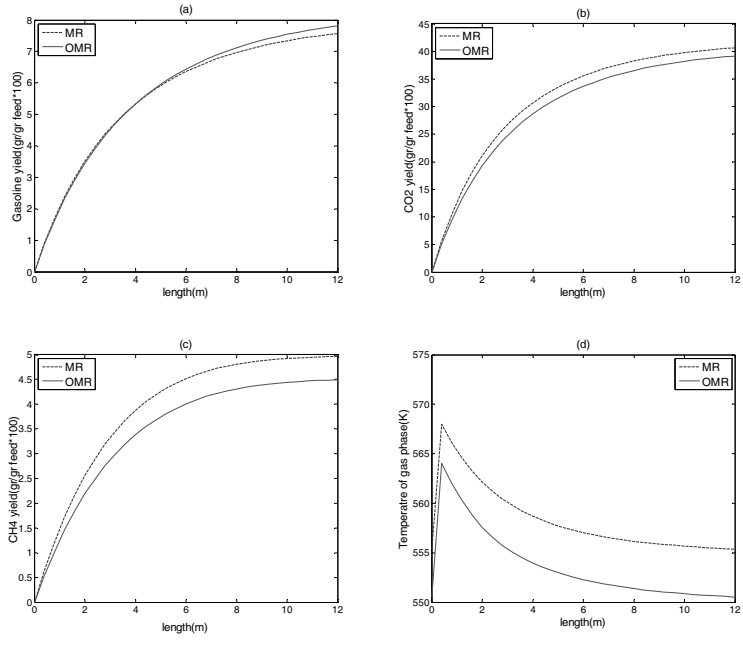


*Figure 2: (a) $C_5^+$ (b) $CO_2$ (c) $CH_4$, yield production profiles and (d) temperature of gas phase along the OMR and MR systems.*

As shown in Fig. 2(d) the temperature control of the OMR is easier in this reactor. For simulation purposes, the maximum temperature for the bifunctional Fe-HZSM5 catalyst to remain active is assumed to be 620 K. As can be seen, in MR system, the temperature of catalyst bed cannot be controlled (i.e., a hot spot is likely) whereas in OMR is achievable.

## 6. Conclusions

A novel membrane configuration for Fischer-Tropsch synthesis was modelled and optimized to increase $C_5^+$ production yield and decrease by products. The potential possibilities of the different configurations of FT reactors were analyzed using one-dimensional packed bed model to obtain the necessary comparative estimates. The mathematical model was validated against the RIPI pilot plant data and then optimized to maximize gasoline production and minimize $CO_2$ yield. The optimization was carried out and the results show there is a favourable profile of FTS products along the optimized OMR system relative to the MR. Optimal catalyst size and temperature profile along the reactor were obtained and 3.181 5 % additional $C5^+$ yield was resulted in optimized system relative to membrane FTS reactor.

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## References

Cagnoli, M.V., Gallegos, N. G., Alvarez, A. M., Bengoa, J. F., Yeramián, A. A., Schmal, M., Marchetti, S. G., 2002, Catalytic CO hydrogenation on potassic Fe/zeolite LTL. Applied Catalysis, 230, 169-176.

Forghani, A.A., Elekaei, H., Rahimpour, M.R., 2009, Enhancement of gasoline production in a novel hydrogen-permselective membrane reactor in Fischer-Tropsch synthesis of GTL technology. Int. J. Hydrogen Energy, 34, 3965-3976.

Hall, KR., 2005, A new gas to liquids (GTL) or gas to ethylene (GTE) technology. Catalysis Today, 106, 243-246.

Marvast, A., Sohrabi, M., Zarrinpashneh, S., Baghmisheh, Gh., 2005, Fischer-Tropsch Synthesis: Modeling and Performance Study for Fe-HZSM5 bifunctional catalyst. Chemical Engineering Technology, 28, 78-86.

Roa, F., Block, M.J., Way, J.D., 2002, The influence of alloy composition on the $H_2$ flux of composite Pd-Cu membranes. Desalination 147, 411-416.

Wang, Y.N., Xu, Y.Y., Li, Y.W., Zhao, Y.L., Zhang, B.J., 2003, Heterogeneous modeling for fixed-bed Fischer-Tropsch synthesis: reactor model and its applications. Chemical Engineering Science 58, 867-875.