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# Real time optimization of steam reforming of methane in an industrial hydrogen plant

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ABSTRACT

The main goal of this research is modeling and real time optimization of an industrial steam methane reformer considering catalyst deactivation. In the first step, the reformer is heterogeneously modeled based on the mass and energy balance equations considering a detailed kinetic model. To prove the accuracy of developed model, the simulation results are compared with the available plant data at steady state condition. In the second step, based on the mechanism of catalyst deactivation, a first order decay model is proposed and the parameters of the model are calculated to minimize the absolute difference between calculated methane conversion and plant data. In the third step, an optimal control problem is formulated to maintain hydrogen production capacity at the desired level. Based on the formulated optimization problem, optimal dynamic trajectories of feed temperature and steam to methane ratio are calculated considering two strategies. Then, the performance of developed optimization procedure is proved considering furnace temperature and feed concentration as disturbance. The simulation results show that operating at the proposed optimal condition increases hydrogen production about 11.6%. In addition, the process emission performance defined as hydrogen to carbon dioxide ratio in the product is 6.72 and 7.03 at the conventional and optimized conditions, respectively.



## Introduction

Syngas as a mixture comprising of hydrogen and carbon monoxide is an important feedstock in refinery and petrochemical complexes. It is used to produce methanol, ammonia, ethylene glycol, and various aldehydes [1]. In addition, syngas is severed as a feedstock to Fischer-Tropsch Synthesis. Although a variety of technologies have been developed based on pure hydrogen as an energy carrier, it is used as feedstock in the hydrogenation and hydrocracking processes in oil refinery units [2,3]. Industrially, hydrogen is produced through steam reforming, partial oxidation and dry reforming of hydrocarbons and coal gasification [4]. The composition of produced syngas varies based on the hydrogen to carbon molecular ratio in the hydrocarbon feed stream and process type. Typically, methane is widely used in the reforming process due to higher hydrogen to carbon ratio compared to other hydrocarbons [5]. In the partial oxidation, a sub-stoichiometric mixture of methane and oxygen reacts catalytically and syngas is produced [6,7]. Steam reforming is an endothermic catalytic reaction that methane and steam react at high temperature in a coil furnace. Auto thermal reforming is an integration of steam reforming and partial oxidation to achieve efficient thermal management [8].

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Although steam methane reforming is more economical compared to the other methods due to high efficiency and low feed cost, finding the optimal condition and catalyst deactivation by sintering, coking and poisoning are the major challenges in the steam reforming process. Catalyst deactivation decreases production capacity gradually. In this regard, many researchers have focused on the process modeling, optimization and intensification of reforming process to improve the production capacity and reformer performance. Alatiqi et al. developed a mathematical model to investigate the performance of steam methane reforming at steady state condition [9]. Comparison between simulation results and plant data proved the accuracy of the developed model and considered kinetic model. Asleshirin et al. developed a homogeneous model for steam methane reforming at dynamic condition [10]. They proposed a second order polynomial equation for catalyst decay and calculated the parameters of the proposed model. Jong et al. modeled an steam methane reformer and investigated the effects of operation parameters on the hydrogen production [11]. The results showed that increasing reactor length, air concentration in the burner fuel and thickness of insulating shield could improve the performance of reformer. Pantoleontos at el. developed a one dimensional model for steam methane reforming and calculated the profile of wall temperature to maximize hydrogen yield [12]. The results showed that applying the optimal wall temperature on the coil tube could improve conversion and hydrogen yield.

For complicated problems, the multi-objective optimization satisfies a number of different objectives simultaneously, and the results are more accurate and real compared to the single objective approach. In this regard, the multi-objective optimization is used to find the optimal operating condition of different process [13]. Sinaei et al. modeled and optimized a steam methane reformer using design of experiment and response surface methodology [14]. The hydrogen production and methane mole fractions were considered as two responses. Temperature, pressure, steam to methane ratio, and hydrogen to methane ratio in the feed stream, and tube wall temperature were selected as the independent factors, and the optimum values of independent factors were calculated. Rajesh et al. developed a multi objective optimization problem to achieve maximum carbon monoxide production and minimum methane conversion [15]. They selected feed temperature, furnace temperature, and steam flow rate as decision variables. The optimal Pareto front was developed by non-sorting genetic algorithm and a single optimal solution was selected from list of alternatives by TOPSIS method. Farsi and Hosseini developed a heterogeneous model for an industrial reformer and investigated the effect of feeding type on the process performance. They developed a multi objective optimization problem to maximize methane conversion and minimize pressure drop [16]. The results showed that hydrogen production is improved about 18.1% in the proposed configuration compared to the conventional process. Rajesh et al. simulated an industrial hydrogen plant at steady state condition [17]. The non-dominated sorting genetic algorithm was employed to optimize the operating condition considering hydrogen production and inlet steam flow rate as the objective functions. Then, Pareto optimal front was obtained at different process conditions.

Currently, membrane separation, thermally coupling and sorption enhanced technologies have been proposed to couple with the reforming process to shift the reforming reactions toward the higher conversion [18]. In this regard, Cruz and Silva developed a mathematical model to compare the performance of conventional and membrane reactors in the reforming process [19]. The results showed that methane conversion and hydrogen yield are significantly enhanced by hydrogen removal from reaction zone through the Pd-based membrane. Abbas et al. simulated the sorption enhanced steam reforming of methane using CaO as $CO_2$ sorbent [20]. The result showed that methane conversion in the proposed and conventional processes approaches to 65% and 24% at the same operating condition, respectively. Aboosadi et al. coupled the steam methane reforming and nitrobenzene hydrogenation reactions in an reactor [21]. The simulation results showed that produced heat through nitrobenzene hydrogenation in the exothermic side could play role of fire box in the conventional process.

Generally, optimization of the operating conditions without considering catalyst deactivation suffers from reliability and results are valid at the start of run when the catalyst is completely active. In this regard, the main goal of this research is modeling and real time optimization of an industrial reformer considering catalyst decay. Based on the mechanism of catalyst deactivation presented in the literature, a decay model is proposed to calculate the catalyst activity during the process run time. Then, an optimal control problem is formulated to fix production capacity at the desired level. Based on the formulated optimization problem the optimal trajectories of feed temperature and steam to methane ratio in the feed stream are obtained during the process run time.

## Process description

Steam reforming of methane is widely used to produce hydrogen in oil refinery and petrochemical complexes. After desulfurization of natural gas in a catalytic reactor, methane is preheated, mixed with superheated steam and feeds to the reformer. The reforming reactions are typically carried out in a furnace over the nickel catalyst. The furnace consists of a radiant section including burners and reforming tubes, and a convection section to recover the waste heat of the flue gases. In the radiant section, the catalyst is loaded in the reforming tubes placed in a row along the furnace. The produced heat in the fire box is transferred to the reforming tubes and supplies the heat of reforming reactions. It should be noted that the use of steam, slightly more than the stoichiometric ratio, improves the rate of reforming reactions and prevents coke build up on the surface of catalyst [15]. The outlet product from reformer feeds into the shift reactors to convert steam and carbon monoxide to hydrogen and carbon dioxide. After steam recovery, the outlet stream enters to the hydrogen separation unit. Amine absorption and PSA treating are two conventional processes to separate hydrogen from product. In the amine absorption process, the aqueous solution of amine and outlet stream from shift convertor feed the top and bottom sections of absorption column, respectively and carbon

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