

An Overview To Development Of Steam Reforming Catalyst for Syngas Production By Sarv Oil & Gas Industries Development Co.

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Abstract

Steam reforming reactions have been so far the main route for the production of synthesis gas and will play a key role in the future hydrogen economy. In recent years, steam reforming plants have been operating quite profitably world wide and rapid growth in H₂ production is expected to continue as a result of the growth of its consumption in car industry. Nickel catalysts are employed as the most conventional catalysts in this process. The demand capacity of the steam reforming catalyst for oil and petrochemical industries is estimated to be about 200 MT/year in Iran, which is expected to be increased in the future. In recent years, Iran has been under trade and investment sanctions which are put to action in case by case basis. So, the local production of this strategic catalyst is of great importance for the oil, petrochemical and even steel industries. Based on these reasons, Sarv Oil & Gas Industries Development Company, the leader in catalyst production in Iran, successfully developed its own technology and produced the steam reforming catalyst in industrial scale. This paper gives a brief overview of production of steam reforming catalyst by Sarv Oil & Gas Industries Development Company.

Key words: Steam Reforming, Nickel Catalyst.

1- Introduction

Synthesis gas (or syngas), a mixture of hydrogen and carbon monoxide is one of the most important feedstocks in the chemical industries. From syngas mixtures having different H₂ /CO ratios, a wide variety of products can be manufactured, Table 1, [1-3].

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There are a number of technologies available to produce syngas. These technologies are summarized in Figure 1. Of the technologies shown in Figure 1, steam methane reforming (SMR) is the most common. In this process light hydrocarbon feedstock and steam are converted in an endothermic reaction over a nickel catalyst. Heat to the reaction is provided in a radiant furnace.

Table 1- Sources of syngas and their applications

H ₂ /CO Ratio	Application
1	Oxoalcohols, polycarbonates, formaldehyde production, Pure CO
2	Methanol synthesis, Fischer-Tropsch synthesis
>3	H ₂ production e.g. for ammonia synthesis

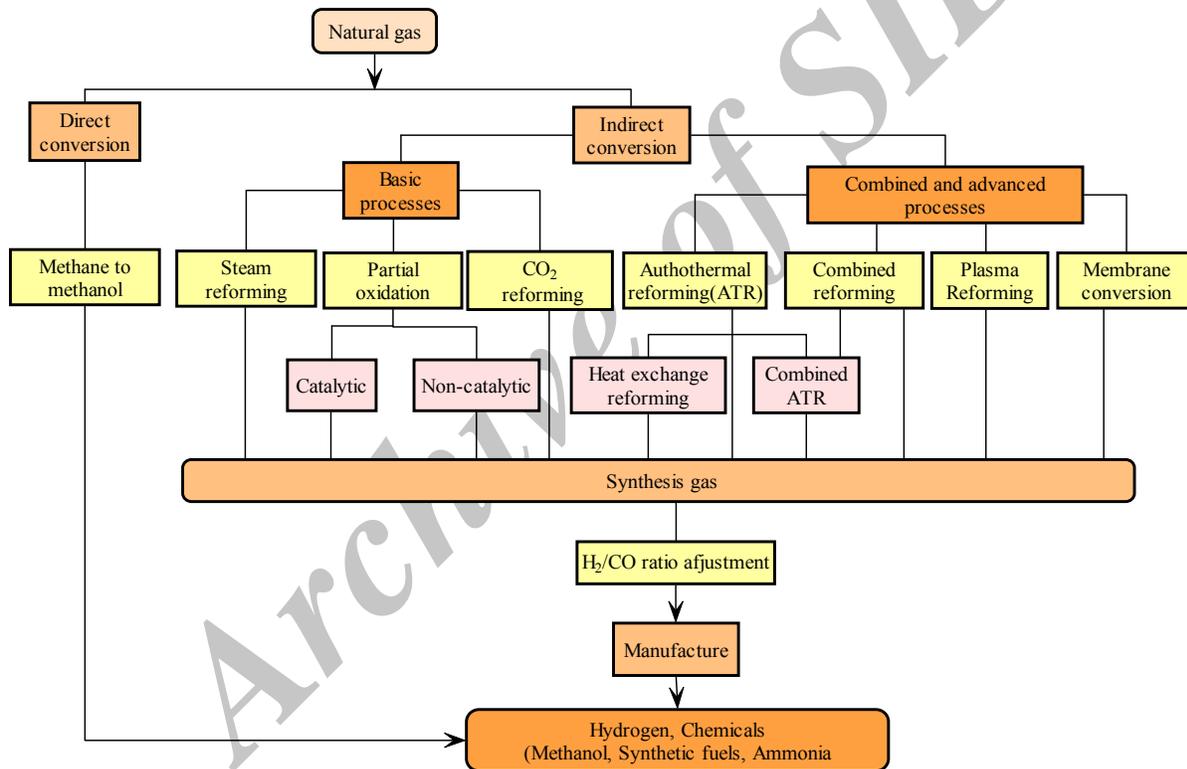


Figure 1- General overview of the routes from hydrocarbons to chemicals.

Steam reforming technology was pioneered in the first quarter of this century by BASF, who developed the basic configuration and engineering of a primary reformer in 1920. The steam methane reforming (SMR) process can be described by two main reactions:



The first reaction is reforming itself, while the second is the water-gas shift reaction. A steam methane reformer produce hydrogen and carbon monoxide by reacting methane with steam over a nickel catalyst at high temperature. The catalyst is contained in tubes located in a fire furnace that provides the large endothermic heat of reaction. In a typical steam reforming process, Figure 2, natural gas is desulfurized, mixed with steam, and preheated to approximately 510 °C before entering the reformer tubes. In the tubes, methane reacts catalytically with steam to produce H₂ and CO [4]. Since steam reforming is an energy-intensive process, efficient heat recovery from both the furnace flue gas and the reformed syngas is essential. For the reforming process, about 40% of the furnace the endothermic heat of reaction absorbs duty. Another 25% of the fired duty is recovered by generating export steam. Of the remaining 35% of the fired duty, approximately 10% is lost to the stack gas, cooling water and heat leaks. After heat recovery, the cooled syngas is treated to remove carbon dioxide. Typically, a chemical solvent such as monoethanolamine or hot potassium carbonate is required to obtain the desired purity. The carbon dioxide is compressed and recycled to the reformer to increase the syngas CO/H₂ ratio [4,5]. This process is extremely productive and has most extensive industrial experience. The synthesis gas produced in this process has the best H₂/CO ratio for hydrogen production applications, but it poses a number of problems: the H₂/CO ratio of the synthetic gas obtained is large, ranging from 3 to 6 and often higher than required, when CO also is to be produced. This process has Highest air emissions and energy consumption is extensive [6,7].

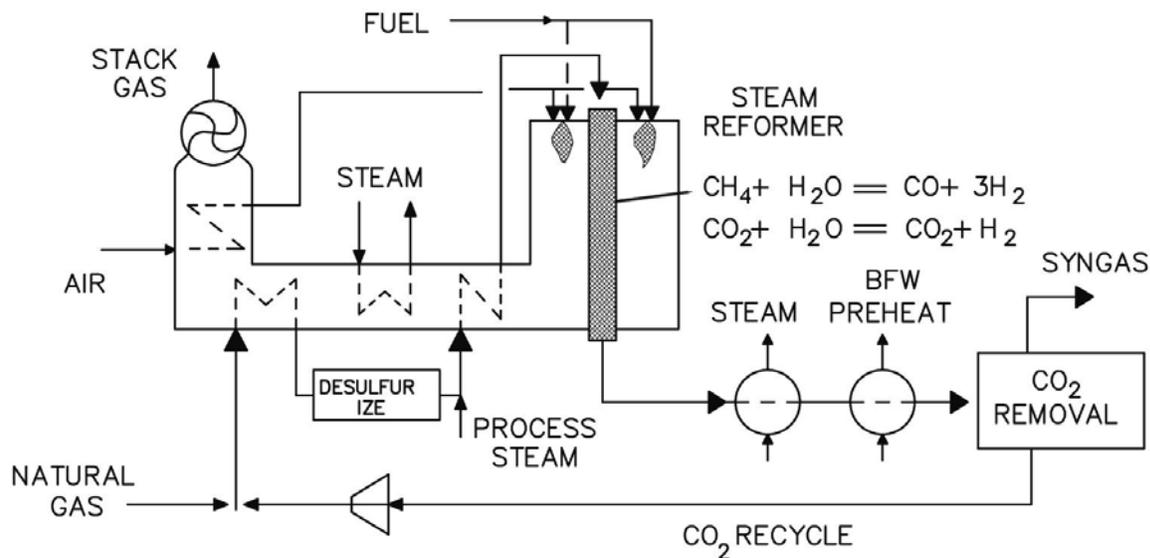


Figure 2- Steam methane reformer for syngas production.

2- Steam Reforming Catalyst

In summary, the operator's requirements to the reformer are: full conversion, which means a close approach to equilibrium at the reformer exit, low tube wall temperatures to ensure long life, constant pressure drop to maintain full process flow equally

distributed through all reformer tubes. To meet these requirements, the catalyst must have sufficient activity resistance to coke formation, and mechanical strength. The metals of group VIII of the periodic system are active for the steam reforming reaction. However, apart from a few exceptions, nickel appears to be the active metal in industrial catalysts. In addition. A great number of oxides have been proposed as promoters for the catalysts to improve either the activity or the ability to prevent formation of coke. In addition to the catalytic function, the mechanical properties of the catalyst are critical. The temperature level and the steam partial pressure restrict the choice of support material for the catalyst.

Most industrial catalysts for tubular reforming are based on ceramic oxides or oxides stabilized by a hydraulic cement. Typical ceramic supports are α -alumina, magnesia, aluminium spinel, and Zirconia fired at temperatures well above 1000°C. The cement type catalysts are normally stabilized by a silica-free binder such as calcium aluminate.

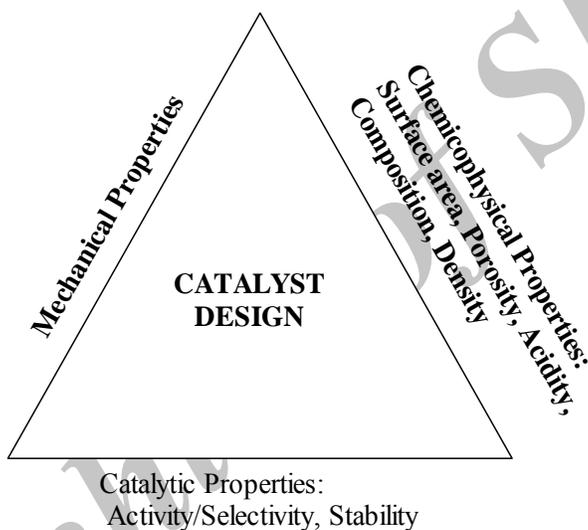


Figure 3- Triangular concept for catalyst design [8].

Richardson [8] introduced the concept of a catalyst design triangle and discussed how the catalyst design is a careful optimization of physical/mechanical, chemical and dynamic properties, Figure 3. Catalyst design is an optimized combination of independent mechanical, chemicophysical and catalytic properties. For example, activity is increased by increasing porosity (improves access to reactants) and surface area (increases available area for reaction), however the surface area decreases with increasing porosity. Moreover, catalyst strength declines to unacceptable levels as porosity increases above 0.5. Sarv steam reforming catalyst has been optimized to have a high mechanical strength, acceptable chemicophysical and catalytic properties. In following the different procedure steps of Sarv steam reforming catalyst production has been reviewed in summary.

3- Steam Reforming Catalyst Production

3-1- Carrier Production

All the raw materials required for the process will be received at the warehouse from suppliers, and stored until required on the plant. In catalyst production plants, firstly the raw materials are analyzed and checked by the quality control department. These raw materials are then prepared so as to facilitate the production of the carrier. The carrier is the base or building block of any heterogeneous catalyst. The raw materials which are used in catalyst production should have a high quality and free of impurities such as silica, sulphates, iron oxide, etc. It is noted that the silica under the operating conditions of the steam hydrocarbon reforming reaction tends to migrate from the catalytic structure and the silica vapor will pass through the reactor into the heat exchanger equipment and there condense and foul the heat exchanger tubes.

The schematic in Figure 4 shows a diagram of the carrier production. The different preparation steps of this diagram have been discussed below.

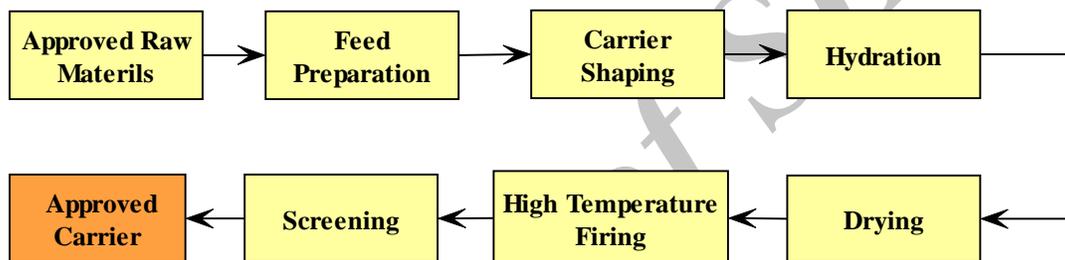


Figure 4- Preparation diagram of the catalyst carrier

In Sarv steam reforming plant, after the quality control, the approved raw materials will be mixed together according to the laboratory formulation (Figure 5a). After mixing, the powder has been sized to be suitable for feeding to a shaping machine (Figure 5b). Usually tableting press has been used for shaping the carriers in steam reforming catalyst. After that, the prepared powder is mixed with a lubricant of a type that is compatible with the catalyst and suitable for the lubrication of the dies and punches in the tableting machine.

Figure 5 shows the different preparation steps of Sarv steam reforming carrier. It is noted that the Sarv steam reforming catalyst is based on calcium aluminate. So after shaping, the raw carriers (Figure 5c) must be steam hardened at elevated temperatures and pressures for a specific period of time. After steam hardening, the carriers are dried (Figure 5e) and then calcined at high temperatures above 1100°C (Figure 5f). After calcination the prepared carriers should be checked from the quality point of view. In this step the mechanical strength, porosity, surface area and other physical properties are determined and approved carrier will be used for the next catalyst preparation step (Figure 5g).

The carriers made by Sarv Oil and Gas Industries Development Company have a multiphase structure. By varying the amount of Ca, one can form various CA_x phases. The most common CA_x phases are monoaluminate (CA), bialuminate (CA_2), and

hexaluminate (CA_6). As indicated in Table 2 the CA_6 phase has the highest melting point, crystal density, porosity, and compressive strength. Thermodynamically, CA_6 is the most stable phase in the CA_x family [9], therefore, the most desirable phase in most of catalytic applications where better porosity, thermal stability, and mechanical strength are beneficial. In Sarv steam reforming catalyst hexaluminate is the major phase and it has all the mentioned advantages above.

Table 2- Properties of various calcium aluminate phases [9].

Phase	Melting Point (°C)	Crystal Density (g/cc)	Porosity (%)	Compressive Strength (Mpa)
$CaO \cdot Al_2O_3$	1600	2.98	5.4	116
$CaO \cdot 2Al_2O_3$	1750	2.91	2.7	172
$CaO \cdot 6Al_2O_3$	1830	3.38	8.1	186



Figure 5- Different preparation steps of carrier production, (a) raw material preparation, (b) shaping, (c) shaped carrier, (d) hydration, (e) drying, (f) high firing temperature, (g) prepared carrier.

3-2- Metal Addition

The simplest and probably the most common procedure for dispersing a catalytic species on a carrier involves impregnating the pre-dried support to incipient wetness with an aqueous solution containing a salt of the catalytic element or elements. Once the carrier is formed and tested for dimensions, strength and other physical properties it is then impregnated with nickel. The nickel is put on the carrier by dipping it in a solution of nickel nitrate. Dipping may be defined as the complete immersion of the carrier in a nickel metal solution for a length of time that ensures maximum pickup of the active metal onto the carrier. Various reforming catalysts have different nickel loadings and these varying levels of nickel are a function of the number of times that the carrier is dipped into the solution, the concentration of the nickel nitrate solution, and the ability of the carrier to absorb nickel at each dip. After each dip the catalyst is calcined and the nickel content is checked to determine what the next dipping procedure should be. The final step in the manufacturing process is to calcine the finished catalyst so as to decompose the residual nitrates from the finished catalyst. Figure 6 shows the different preparation steps of catalyst preparation. The following steps in Sarv steam reforming plant are shown in Figure 7.

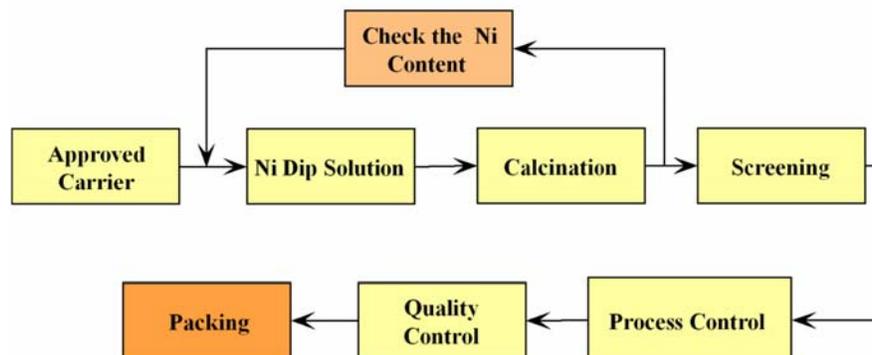


Figure 6- Preparation diagram of the catalyst.



Figure 7- Different preparation steps of catalyst production, (a) approved carriers, (b) impregnation, (c) drying, (d) calcination, (e) calcined catalysts, (f) final product.

4- Chemical and Physical Characteristics

As mentioned before, the base material of Sarv steam reforming catalysts carrier is calcium aluminate cement as binder and support. The major phases of the catalyst carrier are corundum and hibonite ($\text{CaO}(\text{Al}_2\text{O}_3)_6$) and hibonite is in an $\alpha\text{-Al}_2\text{O}_3$ matrix as defined by x-ray diffractometry. Both of these phases are particularly stable under the reaction conditions of steam reforming. In addition, the calcium aluminate as an inert ceramic oxide has an excellent thermal stability at the entire range of temperatures. The catalyst is also stable towards the exposure to condensing steam during start-up or to high temperature steaming. Because of the especial carrier production method, it has a suitable porosity and pore size distribution resulting in a high surface area for the catalyst which improves the catalyst activity. The properties of Sarv steam reforming catalyst are shown in Table 3. It is noted that the Sarv steam reforming catalysts are produced in the shape of 4-hole cylinder with 4 flutes and domed ends, which provide a very low pressure drop and high external surface area which is suitable for enhancing the catalyst activity.

Table 3- Chemical and Physical Characteristics of Sarv steam reforming catalyst

NiO Content (%):	14-15 %
Support Base	Calcium Aluminate
Bulk Density:	0.75 – 0.85 Kg/liter
Cold Crushing Strength (CCS):	90- 100 Kgf
Surface Area (m ² g ⁻¹)	34
Support Pore Volume (Cm ³ g ⁻¹)	450-500
Silica content	Less than 0.1%
Forms:	4-hole Cylinder with 4 flutes and domed ends Diameter: 13 mm Length: 16.4 mm Hole size: 3.2 mm

The catalytic properties of Sarv steam reforming catalyst are compared with those obtained for a standard steam reforming catalyst. The obtained results showed that this catalyst has a comparable catalytic performance with standard catalyst.

Table 4- Catalyst Evaluation Results, GHSV: 2000 h⁻¹, Steam/Carbon: 3, Atmospheric pressure

Temperature (°C)	CH ₄ Slip, mole%		H ₂ , mole%		CO, mole%		CO ₂ , mole%	
	Standard sample	Sarv catalyst	Standard sample	Sarv catalyst	Standard sample	Sarv catalyst	Standard sample	Sarv catalyst
650	4	3.5	74.5	75	10	11	11.5	11.5
750	0.6	0.55	75.5	75.5	16	16	8.6	8.8
850	0.03	0.02	74.8	75.1	19	19	6.8	7

5- Conclusion

Sarv Oil & Gas Industries Development Company successfully developed the second type of its catalyst based on its own technology in industrial scale. The first reforming catalyst is direct reduction of iron catalyst, which is employed in Midrex reformer for production of synthesis gas for reduction of iron oxides. The prepared catalysts were loaded in Midrex reformer of Khoozestan Steel Company (KSC) and the obtained results showed a comparable catalytic performance to commercial catalyst supplied by Süd Chemie. The second type of reforming catalyst as mentioned in this paper is primary steam reforming catalyst, which has been successfully developed by Sarv Oil&Gas Industries Development Co., the leader in catalyst production in Iran. The physical, chemical and catalytic properties of the prepared catalysts led to obtain a catalyst with high activity and stability compare with those obtained for standard steam reforming catalyst. The high mechanical strength, pore volume and specific surface area of the support cause this support to be potentially suitable for steam reforming catalyst preparation.

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