Catalysis Today 145 (2009) 72–75

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Steam reforming and chemical recuperation

J.R. Rostrup-Nielsen *

Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby, Denmark

A R T I C L E I N F O

Article history:
Available online 3 August 2008

Keywords:
Steam reforming
Chemical recuperation
Convective reforming
Hydrogen
Gas turbines
Fuel cells

A B S T R A C T

The high endothermicity of the steam reforming reaction may be used for "chemical" recuperation of high temperature heat representing an alternative to raising steam. Examples are described and the prospects for new reformer concepts are described.

1. Introduction

The steam reforming reaction has been well-described leading to a better understanding of the mechanism at the atomic level [1], the reaction kinetics and also the impact of seconday phenomena [2] such as sintering, carbon formation, and sulphur poisoning. Julian Ross et al. have contributed to this development [3–6].

Steam reforming of natural gas and other hydrocarbons is the preferred route to syngas. The reaction between the two stable molecules, methane and water is strongly endothermic, which is compensated partly for by a positive entropy of reaction. It means that high temperatures are required to achieve maximum conversion.

The reaction is most often carried out in a heated furnace, the tubular reformer, in presence of a nickel catalyst. The catalyst is exposed to severe conditions [2], but in practice there is a large surplus of activity. The product gas is close to equilibrium at the exit temperature.

Tubular reformers are built today for capacities more than 200,000 Nm^3 per hour of hydrogen. The economy of scale is almost linear with total costs related to the number of tubes and burners, etc. It means that autothermal reforming or partial oxidation processes become more economical at very large scale [7] as in GTL (20,000 bpd) and mega-scale methanol plants (10,000 t/d) because the economy of scale of an oxygen plant is more favourable than that of the tubular reformer.

The heat transfer in the tubular reformers takes place primarily by radiation (>95%) from the furnace gas and, in a side wall-fired furnace also from the furnace walls, the remaining being convection [8]. About 50% of the heat input is transferred through the tubes for the reforming reaction and for heating up the gas to the exit temperature. The heat of the flue gas and the process gas is recovered for preheating of feed and combustion air and for raising of steam in a waste heat section. In ammonia plants and other petrochemial plants, the steam can be used to drive the synthesis compressor, but in hydrogen plants, there is little need for steam. Hence, many hydrogen plants have a significant export of steam [9].

The paper deals with possibilities to replace steam production by "chemical recuperation", i.e. using the waste heat for driving the endothermic steam reforming reaction in convective reactors.

2. Convective reforming for hydrogen

It is possible to increase the amount of heat transferred to process gas from about 50% to about 80% when utilizing the heat of hot flue gas for the process by heat exchange [2]. This is achieved in a convective reformer in which the flue gas as well as the product gas is cooled by heat exchange with the process gas flowing through the catalyst beds [10]. This results in a more compact piece of equipment. However the heat exchange is primarily by convection which generally leads to lower heat fluxes (and hence bigger equipment) than in tubular reformers with radiant heat transfer. Hence, the fired reformer remains the most economic solution for large scale steam reforming.

Convective reforming can improve the productivity of the fired reformer by utilising the hot product gas for supplementary heat

---

* Tel.: +45 45 272000; fax: +45 45 272999.
E-mail address: JRN@topsoe.dk.

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.06.019

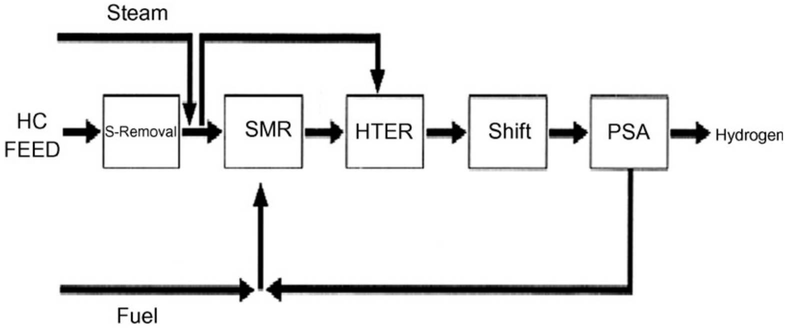

Fig. 1. Hydrogen plant wih chemical recuperation [11]. After desulphurisation of the hydrocarbon feed and addtion of steam, part of the process gas is converted in the tubular reformer (SMR). The other part bypasses the SMR and is added to the convective reformer (HTER) which use the hot exit gas from SMR as heating source. The two streams are mixed before leaving HTER and is passed through a water gas shift reactor before purification of the hydrogen rich gas in a unit for pressure swing adsorption (PSA). The offgas from the PSA unit is used as fuel in the SMR together with additional natural gas.

input to the process, i.e. by "chemical recuperation" of the heat in the process gas instead of raising steam [11]. This can be done in various ways. The product gas may simply be passed through the reformer tube in a bayonet type arrangement, i.e. counter-current to the flow through the catalyst bed. In this way, the capacity of the reformer furnace can be increased by 25% and the steam export reduced by 30% [11].

Another approach [11,12] is the installation of a parallel convective reformer heated by the hot process gas from the tubular reformer as illustrated in Fig. 1.

With this approach, it is possible to increase the capacity of a hydrogen plant with 30% with the same tubular reformer or reducing the steam export by 40%.

3. Chemical recuperation

3.1. Recuperation of process heat

The example of hydrogen plants illustrates the principle of chemical recuperation, i.e. using the heat for driving endothermic chemical reactions instead of raising steam. This principle has been considered also for the recovery of process gas heat in ammonia and methanol plants [13,14] and lately also in syngas units for GTL plants [15]. A scheme for a typical syngas unit for a natural gas based, world scale GTL plant (17,000 bpd) is shown in Fig. 2. Due to the high capacity, it is based on oxygen-blown autothermal reforming. The process heat is recovered in boilers resulting in surplus steam in the plant. By replacing the boilers with a convective reformer, the process heat of the exit gas from the autothermal reformer is used for steam reforming (chemical recuperation) and for preheating the feedgas to the autothermal reactor. This saves large fired preheaters and reduces the oxygen consumption. As shown in Fig. 3, the convective reformer can be in series or in parallel to the autothermal reformer.

3.2. Gas turbines and fuel cells

The heat of the hot exit gas from gas turbines is normally recovered in steam turbines. An alternative could be chemical recuperation.

The combustion temperature for gas turbines is normally controlled by operating with surplus air, but the dilution causes production of entropy and a corresponding loss of exergy or a decrease in the maximum efficiency which can be achieved. One way of solving this problem [16,17]is to use the exhaust heat from the gas turbine for converting the methane feed by the steam reforming reaction to a fuel gas with less heating value per volume and thereby decreasing the demand for dilution as illustrated in Fig. 4 [16,17].

Still, at a turbine inlet temperature, 1350 °C, the benefits of chemical recuperation remains marginal [16], because only 18% of the natural gas is converted into synthesis gas due to thermodynamic constraints in the heat exchange reformer. At a future turbine inlet temperature at 1500 °C, the higher exhaust temperature from the second turbine creates more useful heat for heat exchange reforming and it means that more than 1/3 of the natural

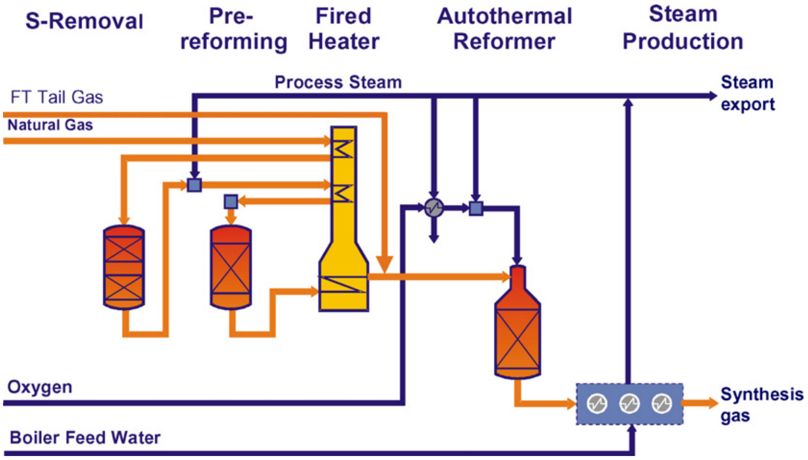

Fig. 2. Syngas for GTL [15]. Natural gas is desulphurised and after addition of steam, the processgas is passed through an adiabatic prereformer (converting higher hydrocarbons) and a fired preheater. Oxygen is added to the burner of the autothermal reformer and the process heat is recovered in a boiler producing steam.

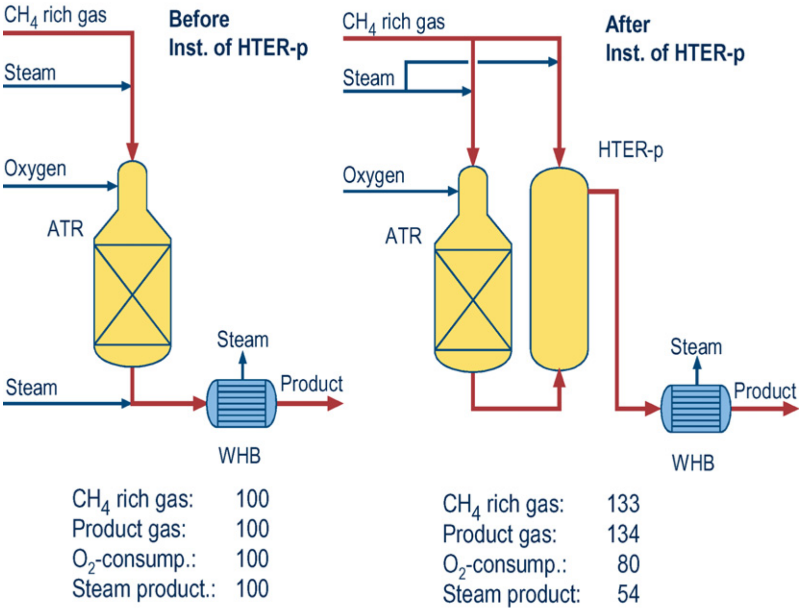

Fig. 3. Syngas for GTL. Gas heated reforming (HTER) in combination with autothermal reforming) [15].

gas can be converted resulting in a similar gain in efficiency [16,17]. A similar increase in efficiency can be achieved by steam injection without reforming reaction, but the amount of steam has to be almost doubled up compared with the steam reforming case.

The thermodynamical constraint is overcome when the convective reformer is replaced with a high temperature fuel cell (SOFC) [18] as shown in Fig. 5. The endothermic conversion of methane to hydrogen is coupled with the exothermal electrochemical reaction of hydrogen and oxygen and the high temperature fuel cell acts as a membrane reformer. In this way, it is possible to achieve almost full conversion of methane by internal reforming in the anode chamber [19].

The exhaust gas from SOFC fuel cell (Fig. 5) provides a hydrogen containing lean fuel gas mixture for the combustion chamber of the gas turbine allowing a more efficient control of the maximum temperature than is achievable by adding the surplus air. In this way, the thermodynamic constraints described above for chemical recuperation are by-passed. Such schemes are claimed to have electric efficiencies close to 70% [20].

The efficiency for coal based IGCC plants can also be increased by coupling the gas turbine with a SOFC fuel cell. The system efficiency is estimated to increase from ca. 40% to above 50% [21]. However, by adding an adiabatic premethanation step prior to the fuel cell [22], the efficiency can be further improved by 2–3% by taking advantage of the internal reforming in the fuel cell.

3.3. Energy transport systems

Chemical recuperation has been considered also for energy transportation systems. This was studied 25–30 years ago in the German ADAM/EVA scheme [23] in which the heat produced in a high temperature, gas cooled nuclear reactor was converted into chemical energy by the steam reforming reaction (EVA). The heat was transferred in a closed loop of helium at 950 °C and 40 bar which was efficient to drive the tubular reformer. The converted syngas was meant to be transported over long distances and converted into high pressure steam by high temperature methanation (ADAM) [24]. Similar schemes are being considered today for converting solar energy produced at remote locations

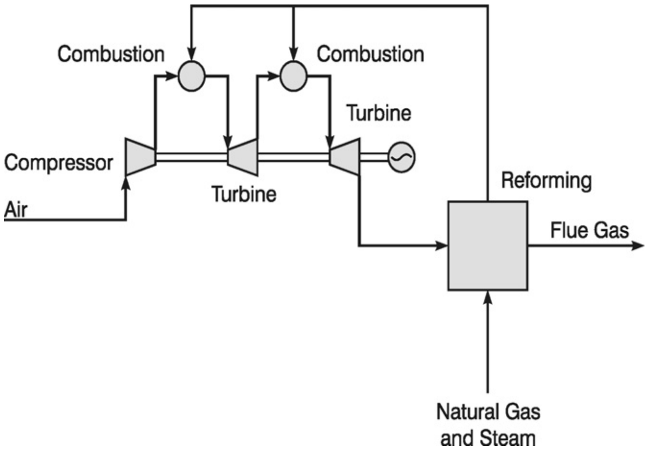

Fig. 4. Chemical recuperation for gas turbines [17]. Steam and natural gas are converted in a convective reformer and the syngas is led to the combuster of the gas turbine. The hot exhaust gas from the turbine is used as heating source for the convective reformer.

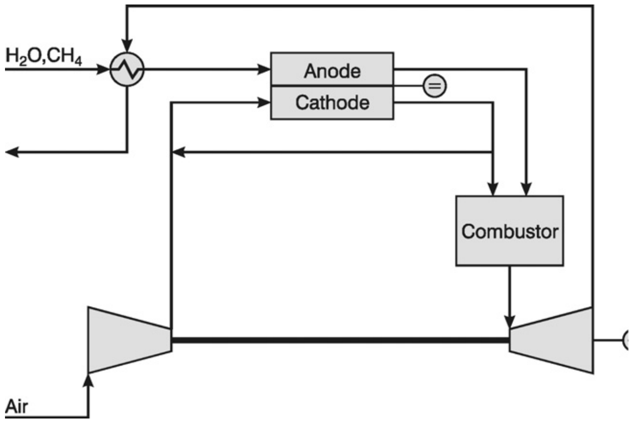

Fig. 5. SOFC and gas turbine cycle [9]. Steam and methane are converted by reforming in the anode chamber and the syngas and the hot and depleted air from the cathode chamber are led to the combuster of the gas turbine. The hot turbine exhaust gas is used for preheating of steam and methane.

into chemical energy by CO_2-reforming of methane [25]. CO_2 is used instead of steam to avoid the problem of raising steam.

The key problem is to transform the heat from the solar receiver to the reforming reaction. One approach has been the use of a sodium heat pipe [25]. Other attempts have applied an integrated receiver [26,27].

4. New reformer concepts

It can be shown that there is a huge surplus of activity in a tubular reformer [9]. High conversion can be achieved at space velocities of the same order of magnitude as reported for CPO ($SV_{C1} \sim 10^6$ vol CH_4 (vol cat)$^{-1}$ h^{-1}) [28]. However, the tubular design imposes constraints on the utilisation of the catalyst. The tube diameter and the total tube surface area are fixed from mechanical design criteria and the constraint from maximum allowable temperature difference over the tube wall. This leaves a large catalyst volume as the dependent parameter (SV = 2000–4000 vol CH_4 (vol cat)$^{-1}$ h^{-1}) [8,29]. As a result the process gas in a tubular reformer is soon close to equilibrium, with the axial temperature gradient being the main driving force for further conversion [8]. The catalyst tubes are filled with large catalyst pellets to minimize pressure drop and improve heat transfer, however, resulting in low catalyst utilization (effectiveness factor) [8]. Convective reforming alows breaking the “tubular constraint” [2,29,30] of the tubular reformer. This may involve the use of catalyzed heat transfer surfaces [30,31] or a split of heat transfer and reaction in a series of adiabatic reactors and heat exchangers [32]. Plate type reformers and multi-channel reformers are being developed for compact units for small scale operation [33]—for instance, for the use in cars, but large scale plants are also being considered [11]. The multi-channel reformer designs are compact with estimated hourly productivities in the order of 1000 Nm^3H_2 (m^3 reactor)$^{-1}$ [2].

The use of “chemical recuperation” may involve cooling down of the process gas through a temperature range with potential for carbon formation from carbon monoxide and attack from metal dusting corrosion [34,35]. This is a potential problem in particular for methanol and GTL plants, but also for hydrogen plants.

The initiation of metal dusting appars to be via the formation of whisker carbon [1,36] as observed also on steam reforming catalysts [1]. However, the limits for metal dusting corrosion are dictated by several parameters and in a complex way. The risk for corrosion is strongly influenced by the selection of construction materials and passivation methods.

5. Conclusions

The established knowledge of the steam reforming reaction has allowed to break the “tubular constraint” of the traditional fired reformer. Convective reforming has created the basis for new reformer concepts which can be applied for “chemical recuperation” of heat taking advantage of the high endothermicity of the reforming reaction. Examples include large scale chemical plants and energy transport systems as well as several scale multichannel reformers. The internal reforming in high temperature fuel cells means higher electric efficiencies. The convective reforming involves the risk of metal dusting corrosion which may limit its application.

References

[1] J.R. Rostrup-Nielsen, J. Sehested, J.K. Nørskov, Adv. Catal. 47 (2002) 65.
[2] J.R. Rostrup-Nielsen, in: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA (Chapter 13.11, pp. 1–24), 2008.
[3] J.R.H. Ross, in: M.W. Roberts, J.M. Thomas (Eds.), Surface and Defect Properties of Solids (Specialists Periodical Reports), vol. 4, The Chemical Society, London, 1974, p. 34.
[4] L.E. Alzarmora, J.R.H. Ross, E.C. Kruissink, L.L. van Reijnen, Chem. Soc., Faraday Trans. I 77 (1981) 665.
[5] K. Seshan, H.W. ten Barge, W. Hally, A.N.J. van Keulen, J.H.R. Ross, Stud. Surf. Sci. Catal. 81 (1994) 285.
[6] D. Tracy, E. Xue, J.H.R. Ross, EUROPACAT 5, Abstract 5-O 10 (2001).
[7] J.R. Rostrup-Nielsen, Catal. Today 63 (2000) 159.
[8] J.R. Rostrup-Nielsen, in: J.R. Anderson, M. Boudart (Eds.), Catalysis, Science and Technology, vol. 5, Springer–Verlag, Berlin, 1984 (Chapter 1).
[9] J.R. Rostrup-Nielsen, T. Rostrup-Nielsen, Cattech 6 (2002) 150.
[10] I. Dybkjær, S. Winter-Madsen, Hydroc. Eng. (November 2004) 23.
[11] J.R. Rostrup-Nielsen, S. Winter-Madsen, Prep. Pap.-Am. Chem. Soc., Div. Pet. Chem. 53 (1) (2008) 82.
[12] S. Winter-Madsen, H. Olsson, Hydroc. Eng. (July 2007) 37.
[13] J.R. Rostrup-Nielsen, I. Dybkjær, L.J. Christiansen, in: H.J. de Lasa (Ed.), NATO ASI Chemical Reactor Technology for Environmentally Safe Reactors and Products, Kluwer Academic Publications, Dortrecht, 1992, p. 249.
[14] E.H. Stitt, in: E.G. Derouane, V. Parmon, F. Lemos, F.R. Ribeiro (Eds.), Proceedings of the NATO ASI “Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities”, Springer, Dortrecht, 2005, p. 185.
[15] P. Bakkerud, J. Gøl, K. Aasberg-Petersen, I. Dybkjær, Stud. Surf. Sci. Catal. 147 (2004) 13.
[16] J.R. Rostrup-Nielsen, Stud. Surf. Sci. Catal. 107 (1997) 473.
[17] J.R. Rostrup-Nielsen, Natural Gas: Fuel or Feedstock, in: E.G. Derouane, V. Parmon, F. Lemos, F.R. Ribeiro (Eds.), Proceedings of the NATO ASI “Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges and Opportunities”, Springer, Dortrecht, 2005 , p. 3 (Chapter 1).
[18] J.R. Rostrup-Nielsen, Chem. Phys. Phys. Chem. 3 (2001) 283.
[19] J.R. Rostrup-Nielsen, L.J. Christiansen, Appl. Catal. A. 126 (1995) 381.
[20] A. Selimovic, J. Pålson, L. Sjunneson, Abstr. Fuel Cell Seminar, Palm Springs, (1998), p. 88.
[21] J. Ferall, A. Depuy, G. Karvountzi, J. Powers, W. Wei, Abstr. Fuel Cell Seminar, Honolulu, (2006), p. 211.
[22] J.B. Hansen, T. Rostrup-Nielsen, J. Pålson, in: Proceedings of the Pittsburgh Coal Conference, Johannesburg, RSA, 2007.
[23] H. Fedders, R. Harth, B. Höhlein, Nucl. Eng. Des. 34 (1975) 119.
[24] H. Harms, B. Höhlein, A. Skov, Chem. Ing. Tech. 52 (1980) 504.
[25] R.B. Diver, J.D. Fish, R. Levitan, M. Levy, E. Meirovitch, H. Rosin, S.A. Paripatyadar, J.T. Richardson, Sol. Energy 48 (1992) 21.
[26] R. Buck, M. Abele, H. Bauer, A. Seitz, R. Tamme, in: D.E. Klett, R.E. Hogan, T. Tanaka (Eds.), “Solar Engineering”, ASME-Book No. G0837, 1994, p. 73.
[27] R. Benito, G.J. Duffy, K.T. Do, R. McNaughton, J.H. Edwards, N. Dave, M. Chensee, C. Walters, International Conference on Greenhouse Gas Control Technologies, Kyoto, Japan, October 1–2, (2002), p. 4.
[28] D.A. Hickman, L.D. Schmidt, Science 259 (1993) 343.
[29] T. Rostrup-Nielsen, Hydroc. Eng. (August 2002) 51.
[30] J.R. Rostrup-Nielsen, Catal. Today 18 (1993) 305.
[31] R.J. Farrouto, Y. Liu, W. Ruettinger, O. Ilinich, L. Shore, T. Giroux, Catal. Rev. 49 (2007) 141.
[32] E.L.C. Seris, G. Abramowitz, A.M. Johnston, B.S. Haynes, Trans. I. Chem. E, Part A Chem. Eng. Res. Dev. 83 (A6) (2005) 619.
[33] A.Y. Tokovich, S. Perry, Y. Wang, D. Qiu, T. la Plante, W.A. Rogers, Chem. Eng. Sci. 59 (2004) 4819.
[34] H.J. Grabke, Mater. Corros. 49 (1998) 317.
[35] J. Chun, Electrochem. Soc. 147 (2000) 3680.
[36] Z. Zeng, K. Natesan, Chem. Mater. 17 (2005) 3794.