

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231392622>

Reduction on Synthesis Gas Costs by Decrease of Steam/Carbon and Oxygen/Carbon Ratios in the Feedstock

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JANUARY 1998

Impact Factor: 2.59 · DOI: 10.1021/ie970402o

CITATIONS

16

READS

12

2 AUTHORS, INCLUDING:



Luca Basini

Research Center for Non Conventional Energy

39 PUBLICATIONS 863 CITATIONS

SEE PROFILE

Reduction on Synthesis Gas Costs by Decrease of Steam/Carbon and Oxygen/Carbon Ratios in the Feedstock

L. Basini[†] and L. Piovesan*

Snamprogetti S.p.A. Research Laboratories, via Maritano 26, 20097 S. Donato Milanese, Milano, Italy

The costs for syngas production at low steam/carbon and oxygen/carbon ratios have been analyzed for simplified process schemes of the main syngas production technologies (steam–CO₂ reforming, autothermal reforming, and combined reforming) and different synthesis gas compositions. The broad analysis arises from experimental indication on the possibility of preventing carbon formation at low steam/carbon and oxygen/carbon ratios in the feedstock by choosing an appropriate catalyst or by introducing small amounts of sulfur compounds in the reactant feed. The analysis is limited to the synthesis gas production step and does not include its downstream processes. The results indicate that technologies at low steam/carbon and oxygen/carbon ratios would have a significant positive impact on synthesis gas costs.

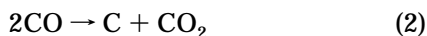
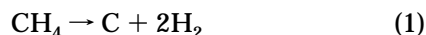
Introduction

The possible routes for finding a solution to the technological and economical challenge of the exploitation of natural gas (NG) include the study of syngas production costs reduction (Gradassi and Green, 1995).

Indeed syngas is an intermediate and its production is a demanding step which absorbs 60–70% of the costs of NG conversion into final products. A reduction of 25% of syngas production costs not only would result in a strong improvement of the existing technologies but also would allow the NG conversion routes to become much more competitive with oil refining (Lange and Tijm, 1996).

The well-established and reliable syngas production technologies have been continuously improved in the past 40 years; comprehensive reviews of existing processes are reported in references (Rostrup-Nielsen (1984a) and Dybkjaer (1995)).

Most of energetic consumption and investment cost in the syngas production technologies are related to the need of avoiding the carbon formation reactions (1) and (2):



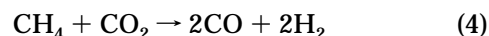
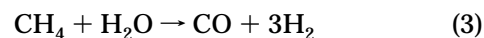
These reactions are inhibited by an appropriate choice of catalyst and by feeding the reactors with reactant mixtures in which high values of O₂/C and/or S/C are maintained (typically O₂/C = 0.65 v/v for autothermal and combined reforming and S/C > 2.5 v/v for steam reforming). Rostrup-Nielsen (1993), Rostrup-Nielsen et al. (1986), and Gadalla and Sommer (1989) have discussed the point in relation to steam–CO₂ reforming catalyzed by a Ni-based catalyst.

This paper examines the effect of different compositions of feedstock in well-established processes on synthesis gas costs. The analysis has been suggested

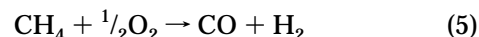
by a number of experimental indications on the possibility of preventing carbon formation at low steam/carbon (S/C) ratios by choosing an appropriate noble metal based catalyst or by introducing small amounts of sulfur compounds into the reactant feed.

Many literature works discuss these points; in particular this study has been stimulated by previous research performed by Richardson and Paripatyadar (1990) and more recently by Basini and Sanfilippo (1995) and by Rostrup-Nielsen and Bak-Hansen (1993) on noble metal based catalysts and by the discussion of sulfur passivated reforming technology reported by Rostrup-Nielsen (1984b), Udengaard et al. (1992), and Dibbern et al. (1986).

For the purposes of this work we will assume that the chemistry of steam–CO₂ reforming of NG whose main component is the methane molecule could be described with the simple equations (3) and (4), which suggest that low S/C feeds should be particularly convenient when low H₂/CO syngas is needed. Nevertheless, the analysis has been extended to the production of synthesis gas mixtures in which the H₂/CO ratio has been varied between 0.88 and 5.1 v/v, finding that the lowering of S/C also reduces the costs of syngas with high H₂ content.



Other syngas production processes which have been examined in this study are the autothermal and combined reforming. Equation 5 combined with eqs 3 and 4 can be taken to represent the chemistry of these processes:



In these cases the cost variation analysis has considered the possibility of reducing both S/C and oxygen/carbon (O₂/C) ratios at very low values, not feasible in the existing plants.

The economic analysis has been focused on doing a comparative study rather than on estimating absolute numbers and, due to its broadness, it has been limited

* Author to whom correspondence is addressed. Tel.: +39 (2) 5205 6870. Fax: +39 (2) 5205 6757. E-mail: laura.piovesan@snampro.atlas.it.

[†] E-mail: luca.basini@snampro.atlas.it.

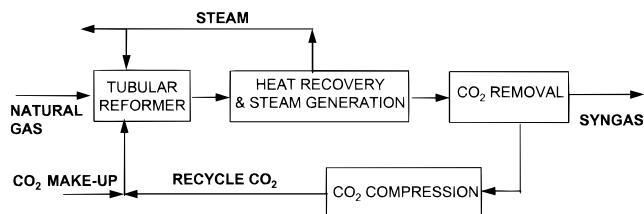


Figure 1. Process flow diagram for steam-CO₂ reforming.

to the synthesis gas production step regardless of the impact on the economics of the downstream users.

In particular it is mentioned that the following assumptions have been adopted in order to disentangle the effects of S/C and O₂/C variations on syngas costs from the effects of other variables: (a) plant capacity has been maintained constant at 300 000 Nm³/h for each examined case; (b) for each considered technology (steam reforming, autothermal reforming, and combined reforming) reactor exit temperatures have been comprised in a ΔT range less than 50 °C, and maximum temperature values have been maintained below the values used in proven technologies; (c) NG has been assumed to contain 100% of methane; (d) the syngas chemistry has been assumed an equilibrium chemistry.

The synthesis gas is an intermediate of many processes and we mention the hydrotreating, the synthesis of ammonia, methanol, acetic acid, and dimethyl carbonate, the Fischer-Tropsch process, the hydroformylation process, and the reduction of iron ores.

Each of these downstream processes presents specific demands with regard to (a) H₂/CO ratios, (b) presence of inert species, and (c) presence of CO₂. For this reason an economic analysis of the integrated synthesis gas production and its downstream utilization would have been too broad. However, since the syngas investment costs represent the 40–70% of overall costs of the above-mentioned processes, this economic analysis can still be considered of some relevance to the overall evaluation of the syngas production–utilization technologies.

The economic analysis has been extended also to cases in which the lowering of S/C and O₂/C ratios has left high CH₄ (≈10% v/v) residue in the product syngas. This high CH₄ residue is too high for many syngas utilization processes but it could be tolerated by innovative large-scale processes for the exploitation of NG sources which could utilize Fischer-Tropsch technologies operating with relatively low H₂/CO ratios and with low limitation on the CO₂ and CH₄ content.

In conclusion it is mentioned that in recent years an innovative catalytic partial oxidation (CPO) process has been proposed by Hickmann and Schmidt (1993) and Choudary et al. (1992), who discovered the possibility of producing syngas from premixed feedstock of oxygen and hydrocarbons at very high space velocity values (GHSV 500 000 h⁻¹ or higher). Although extremely interesting, the CPO process will not be discussed in the present analysis, but we mention that recently Dave and Foulds (1995) have published an economic evaluation devoted to methanol production with CPO.

Process Description and Basis for Evaluations

A process engineering simulator (Aspen Plus) has been used to model three simplified process schemes (see Figures 1–3) for the production of syngas via reforming of natural gas.

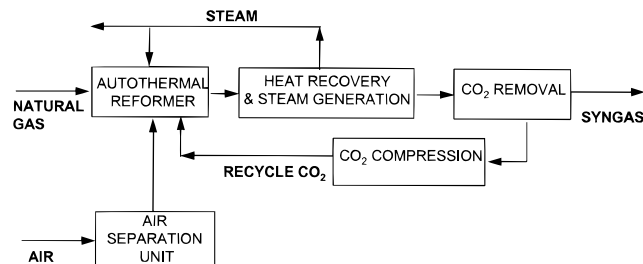


Figure 2. Process flow diagram for autothermal reforming.

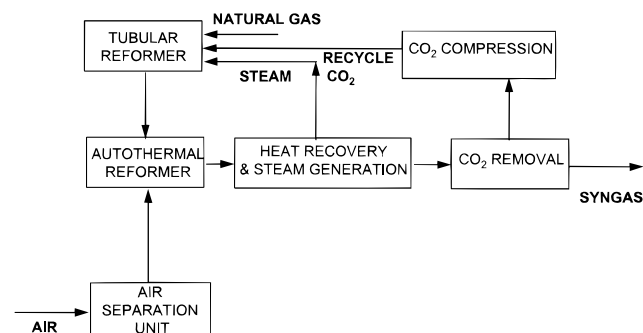


Figure 3. Process flow diagram for combined reforming.

The simplified cost estimation analysis lays on the following assumptions: (a) the natural gas used both as feed and fuel is composed by pure methane available at ambient temperature and at the operating pressure; (b) oxygen (99.5%) is produced at operating pressure by an air separation unit included in the inside battery limits (ISBL) costs and its consumption of power and cooling water are accounted for; (c) process water is purchased at operating pressure and saturation temperature and preheated in a boiler to the temperature required; (d) the CO₂ recycle compressors are steam-driven turbines; (e) catalyst costs have not been included; (f) interest rate of 15% over 10 years in the production cost, for capital recovery is assumed.

Detailed heat and material balance simulations have been performed for all the cases studied. On the basis of the process schemes of Figures 1–3, process equipment has been dimensioned, and its cost has been evaluated on the basis of in-house data and Aspen Plus internal database values. The total investment costs have been calculated referring to the total main equipment installed costs. Raw materials (natural gas, process water, oxygen, and CO₂ makeup) and utilities consumption have been determined from process calculations. Raw materials and the utilities unit cost relate to two different scenarios: U.S. Gulf Coast (natural gas = 1.8 USD/MMBtu) and Saudi Arabia (natural gas = 0.5 \$/MMBtu). In this second scenario the investment has been multiplied by a location factor of 1.2.

Steam-CO₂-Reforming Process Scheme. The scheme is reported in Figure 1. Natural gas is mixed with the required quantity of saturated steam and CO₂ and preheated to 600 °C in the convective section of the reformer. The gas mixture is then fed into heated reformer tubes filled with catalyst in the radiant section of the reformer at an operating pressure of 28 kg/cm². The heat duty for the endothermic reaction is supplied via the complete combustion reaction of fuel natural gas. The product syngas leaves the reformer at a temperature not higher than 900 °C. Heat is recovered from the reactor exit stream by raising high a low-pressure

Table 1. Steam-CO₂ Reforming: Cases Studied (Capacity of 300 000 Nm³/h of an H₂ + CO Mixture)

| | SR/A | SR/B | SR/C | SR/D | SR/E | SR/F | SR/G | SR/H | SR/I | SR/J |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| S/C | 0.62 | 1 | 1 | 1 | 2 | 2 | 3 | 3 | 3.62 | 2.8 |
| H ₂ /CO | 0.88 | 1 | 2 | 3 | 1 | 2 | 2 | 3 | 5.01 | 5 |
| T out ref (°C) | 895 | 850 | 870 | 900 | 850 | 900 | 850 | 850 | 878 | 886 |
| CO ₂ feed (kmol/h) | 6546 | 7566 | 2562 | 605 | 10373 | 3356 | 5593 | 2791 | | |
| CH ₄ feed (kmol/h) | 4207 | 4570 | 5598 | 5650 | 3481 | 3975 | 3980 | 4176 | 3501 | 4027 |
| Dry gas before CO ₂ removal | | | | | | | | | | |
| Kmol/h | 17022 | 18828 | 17096 | 16305 | 20916 | 16269 | 18493 | 17021 | 14674 | 15194 |
| %vol CH ₄ | 5.00 | 6.50 | 13.15 | 14.10 | 2.30 | 3.84 | 3.41 | 4.90 | 0.10 | 0.40 |
| CO ₂ | 16.20 | 22.40 | 8.47 | 3.70 | 33.60 | 13.80 | 24.14 | 16.40 | 0.76 | 0.74 |
| CO | 41.90 | 35.60 | 26.11 | 20.50 | 32.00 | 27.42 | 24.22 | 19.70 | 15.20 | 14.70 |
| H ₂ | 36.80 | 35.50 | 52.27 | 61.60 | 32.00 | 54.94 | 48.23 | 59.10 | 76.10 | 73.50 |
| make up CO ₂ (kmol/h) | 3788 | 3349 | 1114 | | 3345 | 1111 | 1129 | | | |

Table 2. Investment and Production Costs for Steam-CO₂ Reforming

| Scheme | SR-A | SR-B | SR-C | SR-D | SR-E | SR-F | SR-G | SR-H | SR-I | SR-J |
|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|---------------|
| S/C | 0.62 | 1 | 1 | 1 | 2 | 2 | 3 | 3 | 3.62 | 2.8 |
| H ₂ /CO | 0.88 | 1 | 2 | 3 | 1 | 2 | 2 | 3 | 5.01 | 5 |
| a) make-up CO₂ free | | | | | | | | | | |
| Total erected cost | 108.8 | 119.16 | 78 | 68.8 | 132.49 | 85.1 | 106 | 89.9 | 55.83 | 79.54 |
| ISBL | 155.6 | 170.4 | 111.5 | 98.4 | 189.5 | 121.7 | 151.6 | 128.6 | 79.8 | 113.7 |
| OSBL | 70.01 | 76.68 | 50.19 | 44.27 | 85.26 | 54.76 | 68.21 | 57.85 | 35.93 | 51.18 |
| TOTAL FIXED INVESTMENT (MMUS\$ 94) | 225.6 | 247.1 | 161.7 | 142.7 | 274.7 | 176.5 | 219.8 | 186.4 | 115.8 | 164.93 |
| PRODUCTION COST (¢/Nm³ syngas) | | | | | | | | | | |
| Natural gas | 3.071 | 2.954 | 3.111 | 3.135 | 2.897 | 3.425 | 3.456 | 3.382 | 3.890 | 2.647 |
| Process steam | 0.104 | 0.177 | 0.210 | 0.218 | 0.323 | 0.358 | 0.535 | 0.548 | 0.546 | 0.000 |
| RAW MATERIALS | 3.176 | 3.131 | 3.321 | 3.353 | 3.220 | 3.783 | 3.991 | 3.931 | 4.436 | 2.647 |
| UTILITIES | 0.215 | 0.185 | 0.078 | 0.035 | 0.736 | 0.146 | 0.180 | 0.136 | 0.052 | 0.148 |
| BY-PROD. CRED. | -0.382 | -0.423 | -0.430 | -0.597 | -0.505 | -0.430 | -0.390 | -0.542 | -0.967 | -0.462 |
| VARIABLE COSTS | 3.009 | 2.893 | 2.969 | 2.790 | 3.451 | 3.499 | 3.781 | 3.524 | 3.521 | 2.332 |
| FIXED COSTS | 0.352 | 0.377 | 0.276 | 0.252 | 0.411 | 0.293 | 0.345 | 0.305 | 0.220 | 0.279 |
| CAP.RECOVERY | 1.871 | 2.049 | 1.344 | 1.183 | 2.278 | 1.465 | 1.825 | 1.547 | 0.960 | 1.368 |
| TOTAL COST | 5.232 | 5.319 | 4.589 | 4.226 | 6.140 | 5.257 | 5.951 | 5.376 | 4.701 | 3.979 |
| CAPACITY=1.14 MMton/yr | | | | | | | | | | |
| TOTAL ERECTED COST | 83.00 | 94.31 | 78.00 | 80.18 | 104.86 | 85.10 | 106.00 | 104.69 | 75.62 | 108.599 |
| TOTAL FIXED INVESTMENT | 172.10 | 195.55 | 161.73 | 166.25 | 217.43 | 176.45 | 219.79 | 217.07 | 156.80 | 225.18 |
| PRODUCTION COST | 78.756 | 84.061 | 96.486 | 108.524 | 97.100 | 110.682 | 125.280 | 138.092 | 149.070 | 119.980 |
| (\$/ton syngas) | | | | | | | | | | |
| BASE SAUDI ARABIA (\$/ton syngas) | | | | | | | | | | |
| | | | 64.6 | | | 69.13 | 87.45 | | | |
| b) make-up CO₂ from flue gases | | | | | | | | | | |
| TOTAL FIXED INVESTMENT | 308.77 | 322.0 | 191.09 | | 349.52 | 205.82 | 249.52 | | | |
| PRODUCTION COST | 7.47 | 7.32 | 5.28 | | 8.15 | 5.95 | 6.68 | | | |
| (\$/Nm ³ syngas) | | | | | | | | | | |
| CAPACITY=1.14 MMton/yr | | | | | | | | | | |
| TOTAL FIXED INVESTMENT | 236.19 | 405.84 | 191.08 | | 440.53 | 205.82 | 249.51 | | | |
| PRODUCTION COST | 95.41 | 121.78 | 110.75 | | 135.24 | 124.92 | 140.11 | | | |
| (\$/ton syngas) | | | | | | | | | | |

steam. The syngas is then cooled to 50 °C with cooling water and, when necessary, CO₂ is removed by an absorption/stripping step using a MDEA solution. The recovered CO₂ is compressed to the operating pressure and recycled to the reformer. The reformer has been simulated as a nonadiabatic equilibrium reactor (RG-IBBS) in which the composition of the syngas corresponds to equilibrium values at the reaction conditions. A sensitivity analysis has been performed considering S/C ratios in the feed in the range 0.6–3.6 and H₂/CO ratios in the product gas from 0.88 to 5.1.

The CO₂ needed in the feed is partly obtained by recycling the CO₂ washed from the product gas to the reformer. The two following alternatives have then been considered for additional sources of CO₂: (a) make-

up CO₂ is available free in the plant; (b) make-up CO₂ is recovered from the reformer flue gases and the recovery section is included in the ISBL of the plant.

Autothermal-Reforming Process Scheme. The process scheme is shown in Figure 2. Natural gas, saturated steam, and CO₂ are preheated to 300–500 °C and mixed in the reactor burner at a pressure of 30 kg/cm². The autothermal reformer is simulated as an adiabatic equilibrium reactor, and the composition of the syngas produced is the one corresponding to equilibrium at the exit temperature (900–980 °C) determined by the adiabatic heat balance, insofar as the current technological limits for materials allow. The assumptions on the heat recovery and the CO₂ removal sections are the same as those described for the steam-

CO₂-reforming process. Oxygen consumption depends on the heat duty that has to be provided for the endothermic-reforming reaction and on the adiabatic exit temperatures necessary to keep the percentage of methane in the output stream at comparable low values (below 2.5% dry basis) in each examined case.

Combined-Reforming Process Scheme. The combined reforming (Figure 3) features a combination of tubular reforming and autothermal reforming: the gas that leaves the primary reformer at a temperature of 700 °C and with significant unconverted methane is mixed with oxygen and fed to the secondary reformer. At the exit of the secondary reformer the heat recovery and CO₂ removal sections are the same as those described previously.

Results and Discussion

Steam-CO₂ Reforming (SR). Table 1 lists the cases studied, with reference to a capacity of 300 000 Nm³/h of a mixture containing only H₂ + CO.

The case SR/A of Table 1 has been referred to as the HTAS SPARG process discussed by Dibbern et al. (1986). This process can operate at S/C = 0.6 v/v to produce a syngas with H₂/CO = 0.88 v/v.

The cases SR/I and SR/J of Table 1 refer to S/C ratios in the feed respectively of 3.6 and 2.8 v/v to produce a syngas with H₂/CO = 5.0 v/v. These two cases lead to a syngas composition with a stoichiometric number SN (SN see eq 6) of 4.7, which is typical of existing plants for methanol production (see for instance the work by Dybkjaer (1995) for discussion of relationships between S/C and H₂/CO and SN):

$$SN = (H_2 - CO_2)/(CO + CO_2) \quad (6)$$

In the cases SR/A–H of Table 1 the desired H₂/CO ratios are partly obtained by recycling to the production section the CO₂ washed from the reformer exit stream. In the cases SR/I and SR/J, instead, there is no need for CO₂ recycle and CO₂ removal from the product stream is not included.

Table 2 reports the investment and the production costs estimated for the examined steam-CO₂-reforming cases.

The costs SR/A–J have been estimated for a U.S. Gulf Coast scenario at a natural gas price of 1.8 USD/MMBtu. The costs of the cases SR/C, SR/F, and SR/G have also been estimated for a Saudi Arabia scenario at a natural gas price of 0.5 USD/MMBtu. Due to the wide variation in the H₂/CO ratios we have chosen to

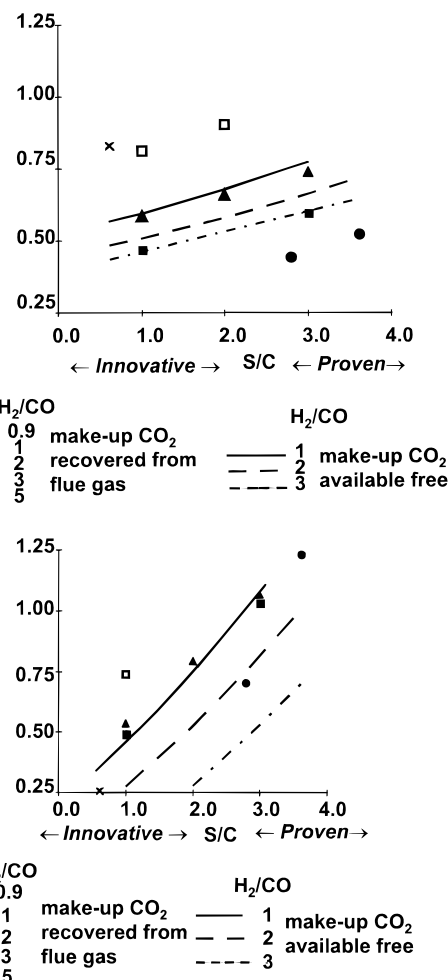


Figure 4. Normalized production cost of synthesis gas from steam-CO₂ reforming vs S/C ratio in the feed. The points refer to the data of Table 2 calculated assuming that makeup CO₂ is recovered from flue gas. The lines result from the regression of the data of Table 2 calculated assuming that makeup CO₂ is available free. The parameters of eq 7 are (a) volumetric basis— $m_2 = 0.86$, $m_1 = 1.14$, $b = 5.51$; (b) weight basis— $m_2 = 1.1$, $m_1 = 1.14$, $b = 64.68$.

express the production costs both on a volumetric and on a weight basis. The volumetric basis production costs are referred to a capacity of 300 000 Nm³/year while the weight basis production costs are referred to a capacity of 1.141 MMt/year. As already mentioned, the capacity considers only pure H₂ + CO mixtures. The results reported in Table 2 referring to the alternative of make-up CO₂ recovered from flue gas have been plotted

Table 3. Autothermal Reforming: Cases Studied (Capacity of 300 000 Nm³/h of an H₂ + CO Mixture)

| Scheme | AR/A | AR/B | AR/C | AR/D | AR/E | AR/F | AR/G | AR/H |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| H ₂ /CO (v/v) | 1 | 1.5 | 2 | 2.4 | 2 | 1 | 2 | 3 |
| S/C | 0.5 | 0.5 | 0.6 | 0.6 | 0.8 | 1.5 | 1.5 | 1.5 |
| O ₂ /C (v/v) | 0.6 | 0.6 | 0.55 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| T _{in} ref (°C) | 360 | 400 | 500 | 250 | 300 | 500 | 480 | 240 |
| T _{out} ref (°C) | 881 | 980 | 992 | 955 | 955 | 796 | 940 | 900 |
| CO ₂ feed (kmol/h) | 6816 | 2262 | 850 | 0 | 1294 | 14664 | 2557 | 467 |
| CH ₄ feed (kmol/h) | 5474 | 5105 | 5034 | 5237 | 5247 | 5734 | 5048 | 5436 |
| Dry gas before CO ₂ removal | | | | | | | | |
| Kmol/h | 18962 | 15414 | 14802 | 14650 | 15468 | 27126 | 16537 | 15961 |
| % vol | | | | | | | | |
| CH ₄ | 2.50 | 1.50 | 2.00 | 2.20 | 2.10 | 2.40 | 1.10 | 2.90 |
| CO ₂ | 26.80 | 11.60 | 7.50 | 6.30 | 11.30 | 48.20 | 17.90 | 13.20 |
| CO | 35.50 | 34.70 | 30.20 | 27.20 | 28.90 | 24.60 | 27.00 | 20.90 |
| H ₂ | 35.20 | 52.20 | 60.20 | 64.30 | 57.70 | 24.80 | 54.00 | 63.00 |
| make up CO ₂ (kmol/h) | 1734 | 474 | 0 | 0 | 0 | 1589 | 0 | 0 |

Table 4. Investment and Production Costs for Autothermal Reforming

| Scheme | AR/A | AR/B | AR/C | AR/D | AR/E | AR/F | AR/G | AR/H |
|--|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| S/C | 0.5 | 0.5 | 0.6 | 0.6 | 0.80 | 1.5 | 1.5 | 1.5 |
| H ₂ /CO | 1 | 1.5 | 2 | 2.4 | 2 | 1 | 2 | 3 |
| O ₂ /C | 0.60 | 0.60 | 0.55 | 0.55 | 0.60 | 0.60 | 0.60 | 0.60 |
| a) make-up CO₂ free | | | | | | | | |
| Total erected cost | 124.1 | 108.42 | 97.4 | 74.63 | 103 | 168.6 | 118 | 97.9 |
| ISBL | 177.46 | 155.04 | 139.28 | 106.72 | 147.29 | 241.09 | 168.74 | 140.00 |
| OSBL | 79.86 | 69.77 | 62.68 | 48.02 | 66.28 | 108.49 | 75.93 | 63.00 |
| TOTAL FIXED INVESTMENT (MMUS\$ 94) | 257.3 | 224.8 | 202.0 | 154.7 | 213.6 | 349.6 | 244.7 | 203.0 |
| PRODUCTION COST (¢/Nm³ syngas) | | | | | | | | |
| Natural gas | 2.837 | 2.652 | 2.648 | 2.731 | 2.643 | 3.077 | 2.753 | 2.827 |
| Process steam | 0.005 | 0.005 | 0.008 | 0.006 | 0.011 | 0.021 | 0.019 | 0.016 |
| RAW MATERIALS | 2.842 | 2.657 | 2.655 | 2.737 | 2.653 | 3.098 | 2.772 | 2.843 |
| UTILITIES | 0.573 | 0.179 | 0.101 | 0.061 | 0.201 | 0.240 | 0.277 | 0.082 |
| BY-PROD. CRED. | 0.000 | 0.000 | 0.000 | -0.093 | 0.000 | 0.000 | 0.000 | -0.028 |
| VARIABLE COSTS | 3.415 | 2.836 | 2.756 | 2.705 | 2.855 | 3.337 | 3.049 | 2.896 |
| FIXED COSTS | 0.409 | 0.370 | 0.343 | 0.286 | 0.357 | 0.520 | 0.399 | 0.344 |
| CAP.RECOVERY | 2.134 | 1.864 | 1.677 | 1.283 | 1.773 | 2.899 | 2.031 | 1.683 |
| TOTAL COST | 5.96 | 5.07 | 4.78 | 4.27 | 4.98 | 6.76 | 5.48 | 4.92 |
| CAPACITY=1.14 MMton/yr | | | | | | | | |
| TOTAL ERECTED COST | 98.19 | 97.67 | 97.40 | 80.25 | 103.00 | 133.44 | 118.00 | 114.01 |
| TOTAL FIXED INVESTMENT | 203.60 | 202.52 | 201.96 | 166.40 | 213.57 | 276.68 | 244.67 | 236.40 |
| PRODUCTION COST (\$/ton syngas) | 93.70 | 93.60 | 100.55 | 98.84 | 104.94 | 107.30 | 115.33 | 125.79 |
| BASE SAUDI ARABIA (\$/ton syngas) | | | | | | | | |
| | | | 71.81 | | 76.38 | | 86.23 | |
| b) make up CO₂ from flue gas | | | | | | | | |
| TOTAL FIXED INVESTMENT | 300.13 | 239.02 | | | | 389.32 | | |
| PRODUCTION COST (¢/Nm ³ syngas) | 7.04 | 5.39 | | | | 7.79 | | |
| CAPACITY=1.14 MMton/yr | | | | | | | | |
| TOTAL FIXED INVESTMENT | 238.12 | 264.73 | | | | 490.96 | | |
| PRODUCTION COST (\$/ton syngas) | 95.83 | 101.91 | | | | 131.42 | | |

(points) in Figure 4a,b in terms of normalized production cost as a function of H₂/CO and S/C ratios. The normalized production costs calculated assuming that CO₂ is available free (Table 2) have been regressed by means of eq 7.

$$\text{production cost} = b(m_1^{\wedge}(\text{S/C}))(m_2^{\wedge}(\text{H}_2/\text{CO})) \quad (7)$$

($\rho^2 > 0.9$) and the resulting exponential curves plotted in Figure 4a,b (lines).

In all the examined cases for a given H₂/CO ratio, the production costs are higher than those for the S/C ratios. For instance, the three cases at H₂/CO = 2 (cases SR/C, SR/F, and SR/G in Tables 1 and Figure 4a) show that lowering the S/C value from 3 to 1 reduces the volumetric production costs 23%, in the assumption that make-up CO₂ is available free in the plant, and 21%, when accounting for make-up CO₂ recovery costs. This variation is related for the 60% to a reduction of variable costs (lower process steam is needed) and for the 40% to a reduction of quantities related to the investment. The investment costs are also reduced by 26% (23% if CO₂ recovery costs are included), and this reduction is

mainly related to the costs of the removal and compression of CO₂. Indeed, at lower S/C ratios the amount of CO₂ required to produce syngas with H₂/CO = 2 is reduced according to equilibria (3) and (4).

The production costs reduction lowering the S/C value from 3 to 1 rises from 23 to 26% when considering the location Saudi Arabia. This difference originates from the lower incidence of variable costs on the production cost (natural gas price = 0.5 USD/MMBtu) together with an increase in capital cost due to a location factor of 1.2.

However the data of Table 1 also indicate that syngas produced with S/C = 1, even though more economical, contains a relevant amount of unconverted CH₄ (≈13% on a dry gas basis) while the cases with S/C = 2 and 3 produce a syngas with a much lower almost the same percentage of CH₄ (≈3% on a dry gas basis). To allow comparisons between cases in which methane conversions are different, the syngas capacities in terms of pure H₂ + CO mixtures have been maintained the same (namely 300 000 Nm³/year or 141.3 MMt/year). It is also noted that the CH₄ percentage in the exit stream would have been reduced by simply raising the reactor

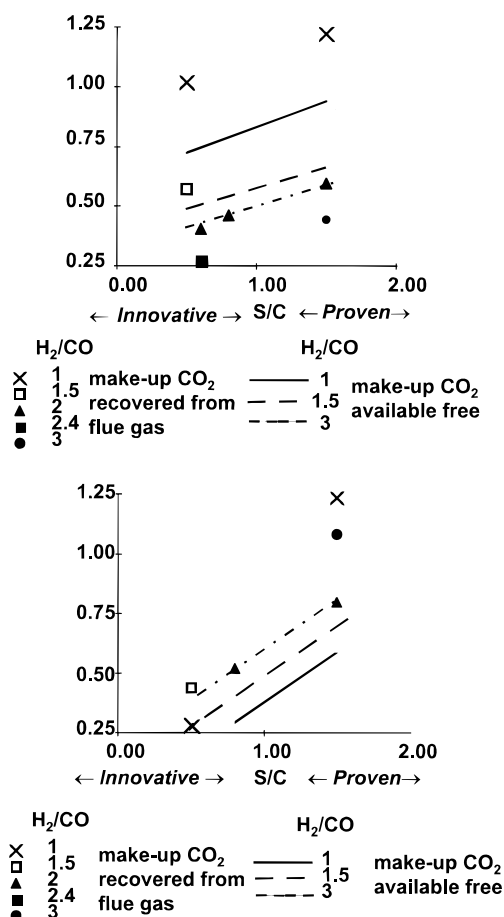


Figure 5. Normalized production costs of synthesis gas from autothermal reforming vs S/C ratio in the feed. The points refer to the data of Table 4 calculated assuming that makeup CO_2 is recovered from flue gas. The lines result from the regression of the data of Table 4 calculated assuming that makeup CO_2 is available free. The parameters of eq 7 are (a) volumetric basis— $m_2 = 0.72$, $m_1 = 1.13$, $b = 7.73$; (b) weight basis— $m_2 = 1.16$, $b = 79.29$.

exit temperatures above 900 °C. Temperatures higher than 900 °C are not normally allowed in steam- CO_2 reformers because they would cause a drastic reduction of reformer tubes lifetime. Literature indication reported by Parks and Schilmoller (1996) suggest that alloys which would allow higher reforming temperatures already exist, but to our knowledge such materials have not yet been used in steam- CO_2 reformers.

High percentages of unconverted methane would increase the costs of some of the main downstream processes for syngas mixtures with $\text{H}_2/\text{CO} = 2$. As

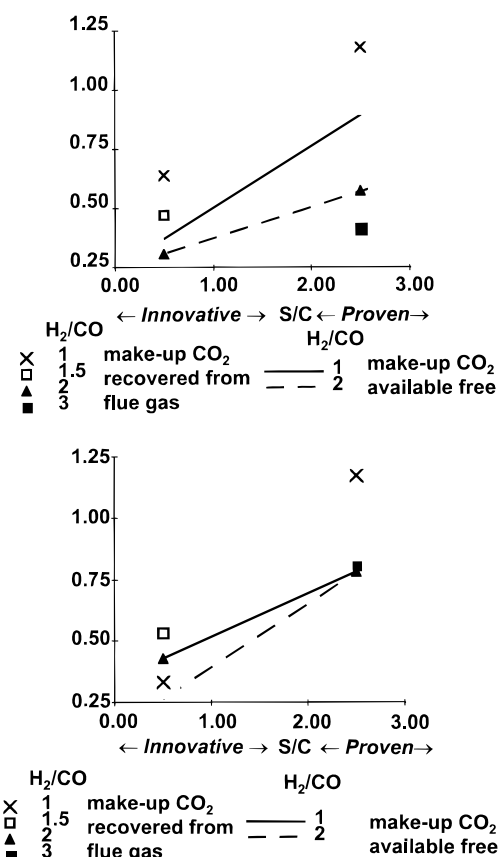


Figure 6. Normalized production costs of synthesis from combined reforming vs S/C ratio in the feed. The points refer to the data of Table 6 calculated assuming that makeup CO_2 is recovered from flue gas. The lines result from the regression of the data of Table 6 calculated assuming that makeup CO_2 is available free. The parameters of eq 7 are (a) volumetric basis— $m_2 = 0.98$, $m_1 = 1.28$, $b = 3.70$; (b) weight basis— $m_2 = 1.30$, $m_1 = 1.27$, $b = 44.87$.

already mentioned in the Introduction paragraph, the discussion of the integration between syngas production and utilization technologies is not the objective of this work; nevertheless, this issue will be further addressed in the conclusion paragraph.

Autothermal Reforming. Table 3 lists the case studied for the autothermal-reforming simplified process scheme. Again the economic analysis has considered cases with production capacities of 300 000 Nm^3/h of $\text{H}_2 + \text{CO}$ mixtures with H_2/CO ratios in the range of 1–3 while the S/C and O_2/C ratios in the feed have been varied respectively between 0.5–1.5 and 0.55–0.6. The values of $\text{O}_2/\text{C} = 0.6$ v/v and S/C = 1.5 v/v can be considered as the lowest limits of current technologies.

Table 5. Combined Reforming: Cases Studied (Capacity of 300 000 Nm^3/h of an $\text{H}_2 + \text{CO}$ Mixture)

| Scheme | CR/A | CR/B | CR/C | CR/D | CR/E | CR/F |
|---|-------|-------|-------|-------|-------|-------|
| H_2/CO (v/v) | 1 | 1.5 | 2 | 1 | 2 | 3 |
| S/C | 0.5 | 0.5 | 0.5 | 2.5 | 2.5 | 2.5 |
| O_2/C (v/v) | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Duty ref. 1° (GCal/h) | 91 | 66 | 54 | 166 | 120 | 112 |
| Tout ref. 2° (°C) | 1068 | 1100 | 1138 | 1015 | 1094 | 1150 |
| CO_2 feed (kmol/h) | 4534 | 1889 | 510 | 10431 | 2766 | 378 |
| CH_4 feed (kmol/h) | 4515 | 4544 | 4551 | 4478 | 4478 | 4475 |
| Dry gas (kmol/h) | 15781 | 14500 | 14000 | 21535 | 16185 | 14908 |
| Dry gas before CO_2 recovery (% vol) | | | | | | |
| CH ₄ | 0.20 | 0.40 | 0.50 | < 0.1 | < 0.1 | < 0.1 |
| CO_2 | 14.80 | 7.10 | 3.80 | 37.70 | 17.10 | 10.00 |
| CO | 42.40 | 36.90 | 31.90 | 31.50 | 27.60 | 22.50 |
| H_2 | 42.50 | 55.50 | 63.80 | 30.70 | 55.20 | 67.40 |
| make up CO_2 (kmol/h) | 2198 | 860 | 0 | 2312 | 0 | 0 |

Table 6. Investment and Production Costs for Combined Reforming

| | CR/A | CR/B | CR/C | CR/D | CR/E | CR/F |
|--|---------------|---------------|---------------|---------------|---------------|---------------|
| S/C | 0.5 | 0.5 | 0.5 | 2.5 | 2.5 | 2.5 |
| H ₂ /CO | 1 | 1.5 | 2 | 1 | 2 | 3 |
| O ₂ /C | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| a) with make-up CO₂ free | | | | | | |
| Total erected cost | 128.25 | 99.95 | 89.8 | 187.1 | 140.6 | 116.25 |
| ISBL | 183.40 | 142.93 | 128.41 | 267.55 | 201.06 | 166.24 |
| OSBL | 82.53 | 64.32 | 57.79 | 120.40 | 90.48 | 74.81 |
| TOTAL FIXED INVESTMENT (MMUS\$ 94) | 265.93 | 207.25 | 186.20 | 387.95 | 291.53 | 241.04 |
| PRODUCTION COST (¢/Nm³ syngas) | | | | | | |
| Natural gas | 1.614 | 2.256 | 2.369 | 3.108 | 2.823 | 2.750 |
| Process steam | 0.003 | 0.004 | 0.006 | 0.028 | 0.028 | 0.021 |
| RAW MATERIALS | 1.617 | 2.260 | 2.375 | 3.136 | 2.851 | 2.771 |
| UTILITIES | 0.062 | 0.076 | 0.083 | 0.524 | 0.276 | 0.116 |
| BY-PROD. CRED. | -0.209 | -0.345 | -0.528 | -0.744 | -0.904 | -0.960 |
| VARIABLE COSTS | 1.470 | 1.991 | 1.930 | 2.916 | 2.223 | 1.927 |
| FIXED COSTS | 0.427 | 0.349 | 0.332 | 0.573 | 0.458 | 0.390 |
| CAP.RECOVERY | 2.205 | 1.719 | 1.546 | 3.217 | 2.420 | 1.999 |
| TOTAL COST | 4.102 | 4.059 | 3.808 | 6.706 | 5.102 | 4.315 |
| CAPACITY=1.14 MMton/yr | | | | | | |
| TOTAL ERECTED COST | 101.51 | 90.04 | 89.80 | 148.10 | 140.60 | 135.38 |
| TOTAL FIXED INVESTMENT | 210.5 | 186.7 | 185.7 | 307.1 | 291.5 | 280.7 |
| PRODUCTION COST (\$/ton syngas) | 66.07 | 75.46 | 80.16 | 107.28 | 107.41 | 109.09 |
| BASE SAUDI ARABIA (\$/ton syngas) | | | | | | |
| | | | 60.51 | | 92.12 | |
| b) make-up CO₂ from flue gas | | | | | | |
| TOTAL FIXED INVESTMENT | 318.29 | 230.83 | | 442.61 | | |
| PRODUCTION COST (¢/Nm ³ syngas) | 5.44 | 4.6 | | 8.17 | | |
| CAPACITY=1.14 MMton/yr | | | | | | |
| TOTAL FIXED INVESTMENT | 252.54 | 255.66 | | 557.86 | | |
| PRODUCTION COST (\$/ton syngas) | 71.47 | 87.57 | | 139.06 | | |

The results of the sensitivity analysis are reported in Table 4. Figure 5a,b shows the variations of normalized production costs vs S/C ratio in the feed. Cost analysis has been made by considering the make-up CO₂ as available free in the plant (lines in Figure 5) or by including the recovery costs of make-up CO₂ from the flue gas (points in Figure 5). The results of Table 4 show that only cases AR/A, AR/B, and AR/F need to import extra CO₂, in relatively low amounts, to achieve H₂/CO ratios between 1 and 1.5 v/v.

As for steam-CO₂ reforming, investment and production costs decrease significantly when the S/C is reduced, keeping constant O₂/C and H₂/CO ratios. In the case of synthesis gas with H₂/CO = 2 the investment and production costs are reduced respectively by 18 and 13%, lowering the S/C from 1.5 to 0.6 and the O₂/C from 0.6 to 0.55 v/v.

Combined Reforming. Table 5 lists the cases studied for the combined-reforming process scheme: two different ratios of S/C in the feed have been evaluated (2.5 and 0.5) to produce syngas at ratios of H₂/CO in the range 1–3. The O₂/C ratio in the feed is assumed equal to 0.5 v/v. The results of cost estimate analysis are reported in Table 6.

It can be pointed out that cost variations are more relevant than those in the other reforming technologies. The syngas with H₂/CO = 2 v/v has fixed investment costs which range from 291.5 to 186 MMUS\$ (36% less) if the S/C varies from 2.5 to 0.5, while production costs

Table 7. Main Operating Parameters of Proven Technologies

| | S/C | O ₂ /C | P (kg/cm ²) | T _{out} 1° reformer | T _{out} 2° reformer | CH ₄ % residue (dry gas basis) |
|----|-----|-------------------|-------------------------|------------------------------|------------------------------|---|
| SR | 3 | | 28 | 850 | | 3–4 |
| AR | 1.5 | 0.6 | 30 | | 800–900 | 2 |
| CR | 2.5 | 0.5 | 30 | 700 | 1100 | 0.1–2 |

Table 8. Main Operating Parameters of Innovative Technologies (Low S/C and O₂/C)

| | S/C | O ₂ /C | P (kg/cm ²) | T _{out} 1° reformer | T _{out} 2° reformer | CH ₄ % residue (dry gas basis) |
|----|-----|-------------------|-------------------------|------------------------------|------------------------------|---|
| SR | 1 | | 28 | 850–900 | | 6–14 |
| AR | 0.5 | 0.6 | 30 | | 880–990 | 2 |
| CR | 0.5 | 0.5 | 30 | 700 | 1100 | 0.1 |

are reduced from 5.1 to 3.8 c/Nm³ (26% less) with no need of make-up CO₂.

Figure 6a,b gives the trends of normalized production costs vs S/C ratio in the feed for different H₂/CO ratios in the product on a volumetric and weight basis. The points in Figure 6 are relative to the data of Table 5, referring to the alternative of CO₂ recovered from flue gas. The lines in Figure 6 have been obtained with a regression of data presented in Table 5, referring to the alternative of CO₂ available free in the plant.

Comparison among Reforming Technologies Costs. In Tables 7 and 8 are summarized the main operating parameters that we assume, for the purposes

Table 9. Comparison of Investment and Production Costs for Proven and Innovative Technologies (Low S/C and O₂/C)

| INVESTMENT (MMUS\$) | | | | PRODUCTION COSTS (c/Nm ³) | | | |
|-------------------------|----------------------|----------------------|----------------------|---------------------------------------|----------------------|----------------------|----------------------|
| PROVEN TECHNOLOGIES | | | | PROVEN TECHNOLOGIES | | | |
| | H ₂ /CO=1 | H ₂ /CO=2 | H ₂ /CO=3 | | H ₂ /CO=1 | H ₂ /CO=2 | H ₂ /CO=3 |
| SR | | 249 | 186 | SR | | 6.7 | 5.4 |
| AR | 389 | 245 | 203 | AR | 7.8 | 5.5 | 4.9 |
| CR | 442 | 292 | 241 | CR | 8.2 | 5.1 | 4.3 |
| INNOVATIVE TECHNOLOGIES | | | | INNOVATIVE TECHNOLOGIES | | | |
| | H ₂ /CO=1 | H ₂ /CO=2 | H ₂ /CO=3 | | H ₂ /CO=1 | H ₂ /CO=2 | H ₂ /CO=3 |
| SR | 322 | 191 | 142 | SR | 7.3 | 5.3 | 4.2 |
| AR | 300 | 202 | | AR | 7.0 | 4.8 | |
| CR | 318 | 186 | | CR | 5.4 | 3.8 | |

of the present work, as representative parameters for proven and for innovative technological solutions.

The estimated costs, for the capacity of 300 000 Nm³/h of H₂ + CO gas mixture, have been summarized in Table 9. In order to compare the different technologies on the same basis, additional costs for make-up CO₂ are accounted for in all cases in the darkened areas.

H₂/CO = 1 v/v Cases. Autothermal reforming has the smallest investment costs both for innovative and proven technologies: even if its oxygen demand, and therefore the cost of the air separation unit (included in the ISBL) is higher than the combined reforming one, it can still enjoy the benefits of a cheap reactor system and of a smaller CO₂ removal section. Autothermal reforming also has the lower production costs if the S/C and O₂/C values are maintained in the range of proven technologies. However, combined reforming benefits more than any other technology from the possibility of reducing S/C and O₂/C ratios and has the lower production costs in the innovative conditions.

H₂/CO = 2 v/v Cases. In the conditions presently adopted by proven technologies, steam-CO₂ reforming and autothermal reforming have lower and comparable investment costs while combined reformer results in a more capital intensive technology. However the low consumption and the higher thermal efficiency of combined reforming allow one to reach the lowest syngas production costs even at S/C and O₂/C values already available in proven technologies. The advantages of combined reforming over steam-CO₂ reforming and autothermal reforming become much more evident if S/C and O₂/C values in the feeds are reduced at the values we defined as innovative. In this case combined reforming would benefit from lower investments and much lower production costs than the other syngas production technologies.

H₂/CO = 3 v/v Cases. Table 9 shows that also at H₂/CO = 3 v/v both investment and production costs of steam CO₂ reforming are lowered by decreasing the amount of steam introduced in the feeds. However, according to the equilibria syngas production reactions (3)–(6) the reduction of S/C ratios below the limits characteristic of proven technologies (see Table 8) would not allow one to produce a syngas with H₂/CO = 3 v/v at the exit of combined- and autothermal-reforming reactors. These last technologies would demand a shift converter to increase the H₂/CO ratio. This step would not necessarily cause a dramatic increase of syngas production costs; however, the discussion of this item is beyond the limits of the present work.

Conclusions

The comparative economical analysis has shown that syngas investment and production costs are strongly

affected by S/C and/or O₂/C values. If these ratios are varied below the limits currently feasible, the syngas costs would be strongly reduced particularly when low H₂/CO ratios are needed. The reduction of such ratios would be allowed by innovative catalysts particularly inactive toward carbon formation reactions (noble metal based catalysts) or, in the steam-CO₂-reforming case only, by process conditions in which carbon formation on conventional Ni-based catalysts, is inhibited with small amounts of sulfur compounds in the feedstock.

The costs of the three different technologies, based on a capacity of 300 000 Nm³/year and assuming that no CO₂ is present in the natural gas, have also been compared showing that combined reforming allows the strongest relative reductions of the production and investment costs by lowering the S/C and O₂/C. Combined reforming is also by far the innovative technology more favored for a syngas production in which H₂/CO = 2 v/v. Autothermal is less capital intensive than combined reforming for the production of H₂/CO = 1 v/v; however combined reforming still maintains the lowest production costs. Steam-CO₂-reforming technology has the highest variable costs, particularly at low H₂/CO ratios; these costs are related to the high fuel consumption in the reformer furnace and to the strong need for CO₂ import, which implies high consumption of steam for turbines and of cooling water in the CO₂ removal section.

In many cases the possible cost reductions have been estimated around 25%; we consider that such reductions strongly motivate innovative solutions concerning partial filling of the reformer tubes with innovative noble metal based catalysts or concerning sulfur passivated reforming. These technologies could also be applied in exploiting economically gas fields where the natural gas has a high content in CO₂ (>10%), as it happens in Indonesia or in some Saudi Arabia locations.

The impact of S/C and O₂/C reductions on the economics of the downstream processes has not been included in this study. Indeed the specific requirements of each downstream process in terms of syngas quality would have resulted in a considerably broader and more complex analysis. Nevertheless, some general indications can be drawn.

Presented data indicate that the economic advantage would be particularly significant for those conversion processes demanding a CO-rich syngas, such as oxo-synthesis conversion, iron ore reduction, acetic acid synthesis, and the hydroformylation process. The Fischer-Tropsch process, requiring an H₂/CO ratio of 2 and operating at a relatively low pressure (ca. 2–3 MPa) with low limitation on CH₄ and CO₂ content, should also take advantage of S/C and O₂/C reduction.

Syngas production processes operating at high pressure (>5 MPa) and integrated with syngas conversion

processes with stringent limitations on CH₄ residue (such as the NH₃ processes) would be instead penalized by the reduction of S/C and O₂/C ratios at constant H₂/CO, since high unconverted methane percentages would significantly increase compression and recycle costs. Alternatively higher temperatures than those reached in conventional tubular reactors for steam-CO₂ reforming would be necessary to reduce the methane residue.

Methanol production processes, with required ratios in the feed (H₂-CO₂)/(CO + CO₂) and CO₂/CO respectively higher than 1.9 and 0.1, would need a case by case study in order to evaluate the impact of the S/C and O₂/C reductions on the overall economy, mainly because many alternative process schemes and technologies are possible. For MeOH plants with a capacity of 3000 MTPD which demand a syngas feedstock of 300 000 Nm³/year, the utilization of a low S/C, O₂/C combined-reforming technology would be particularly convenient because it would allow one to operate the primary reformer at relatively low exit temperatures, leaving relatively high CH₄ residue in the exit gas which could be reduced in the secondary reforming.

Literature Cited

- Basini, L.; Sanfilippo, D. Molecular Aspects in Syngas Production: the Steam CO₂ Reforming Reaction Case. *J. Catal.* **1995**, *157*, 62.
- Choudary, V. R.; Mamman, A. S.; Sansare, S. D. Selective Oxidation of Methane to Carbon Monoxide and Hydrogen over Ni/MgO at Low Temperatures. *Angew. Chem. Int. Ed. Engl.* **1992**, *9*, 31.
- Dave, N.; Foulds, G. A. Comparative Assessment of Catalytic Partial Oxidation and Steam Reforming for the Production of Methanol from Natural Gas. *Ind. Eng. Chem. Res.* **1995**, *34*, 1037.
- Dibbern, H. C.; Olesen, P.; Rostrup-Nielsen, J. R.; Tottrup, P. B.; Udengaard, N. R. Make Low H₂/CO Syngas Using Sulfur Passivated Reforming. *Hydrocarbon Process.* **1986**, January, 72.
- Dybkjaer, I. Tubular Reforming and Autothermal Reforming of Natural Gas—an Overview of Available Processes. *Fuel Process. Technol.* **1995**, *42*, 85.
- Gadalla, A. M.; Sommer, M. E. Synthesis and Characterization of Catalysts in the System Al₂O₃-MgO-NiO-Ni for Methane Reforming with CO₂. *J. Am. Ceram. Soc.* **1989**, *72* (4), 683.
- Gradassi, M. J.; Green, N. W. Economics of Natural Gas Conversion Processes. *Fuel Process. Technol.* **1995**, *42*, 65.
- Hickmann, D. A.; Schmidt, L. D. Production of Syngas by Direct Catalytic Oxidation of Methane. *Science* **1993**, *259*, 343.
- Lange, L. P.; Tijm, P. J. A. Processes for Converting Methane to Liquid Fuels: Economic Screening through Energy Management. *Chem. Eng. Sci.* **1996**, *51*, 2379.
- Parks, S. B.; Schillmoller, C. M. Use Alloys to Improve Ethylene Production. *Hydrocarbon Process.* **1996**, March 56.
- Richardson, J. T.; Paripatyadar, S. A. Carbon Dioxide Reforming of Methane with Supported Rhodium. *Appl. Catal.* **1990**, *61*, 293.
- Rostrup-Nielsen, J. R. Catalytic Steam Reforming. In *Catalysis Science and Technology*; Anderson, J. R., Boudardt, M., Eds.; Springer-Verlag: Berlin/New York/Tokyo, 1984a; Vol. 5.
- Rostrup-Nielsen, J. R. Sulfur-Passivated Nickel Catalysts for Carbon-Free Steam Reforming. *J. Catal.* **1984b**, *85*, 31.
- Rostrup-Nielsen, J. R. Production of Synthesis Gas. *Catal. Today* **1993**, *18*, 305.
- Rostrup-Nielsen, J. R.; Bak-Hansen, J. H. CO₂-Reforming of Methane over Transition Metals. *J. Catal.* **1993**, *144*, 38.
- Rostrup-Nielsen, J. R.; Christiansen, L. J.; Bak-Hansen, J. H. Activity of Steam Reforming Catalysts: Role and Assessment. *Appl. Catal.* **1986**, *43*, 287.
- Undengaard, N. R.; Bak-Hansen, J. H.; Hanson, D. C.; Stal, J. A. Sulfur Passivated Reforming Process Lowers Syngas H₂/CO Ratio. *Oil Gas J.* **1992**, March 9, 62.

Received for review May 30, 1997

Revised manuscript received October 9, 1997

Accepted October 10, 1997[®]

IE9704020

[®] Abstract published in *Advance ACS Abstracts*, December 1, 1997.