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Issues in H_2 and synthesis gas technologies for refinery, GTL and small and distributed industrial needs

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Abstract

H_2 and synthesis gas have been extensively utilised for more that 70 years in chemical and refinery industries. Their uses are becoming today more complex being influenced by strategic, political, economic and sustainability considerations. Issues that would benefit from innovations in the synthesis gas production concern the: (a) clean fuel production and the heavy residues utilisation, (b) the gas to liquid initiatives and (c) the desired but not yet accomplished electric energy production with fuel cells. The technological needs will be examined and their accomplishment will be discussed considering the utilisation of the short contact time–catalytic partial oxidation technologies.

Keywords: Hydrogen and synthesis gas; Reformer; Short contact time–catalytic partial oxidation; Energy production; Gas to liquids; Hydrotreating; Fuel cells

1. Introduction

H_2 and synthesis gas have major utilisation in refining, in the production of ammonia, methanol, formaldehyde, acetic acid and oxoalcohols. Indeed the synthesis gas, made from coke, was also distributed in the large cities as "Town Gas" for cooking, heating and lighting but being dangerously CO rich it has been replaced with natural gas (NG).

In more recent years the synthesis gas, produced from coal; petroleum coke and deasphalter bottoms, has been utilised for feeding large Integrated Gas Turbine Combined Cycles (IGCC) producing electric energy (E.E.) [1]. Relevant initiatives are also ongoing for realising via-syngas gas to liquid (GTL) processes converting NG into high quality energy vectors (gasoils, naphta, methanol and dimethylether) [2]. In conclusion there is a remaining but still sounded hope for the development of reliable fuel cell (FC) technologies [3] requiring H_2 or synthesis gas fuels.

Consequently, the H_2 and synthesis gas mixtures are assuming the role of secondary energy vectors. Fig. 1 concerns this point and shows, in a simplified scheme, how the pool of the primary energy vectors (hydrocarbons, coke, fissile fuels and renewable fuels) can be transformed into thermal, mechanical and electric energy through the intermediate formation of H_2 and synthesis gas.

Briefly, it is noted that the parallel and integrated energy production network would introduce chances for obtaining strategic, economic and environmental advantages. Strategic advantages would follow from the reduction of the vulnerability of the energy production and distribution chain. Linked economic and environmental advantages would follow from the possibility of utilising a two step technology chain allowing a mild environmental impact, particularly at the energy production sites and even when low quality primary energy sources would be utilised.

The discussion of these issues is far outside the scope of this short and simple work that focalises instead on the possible technological innovations for improving H_2 and synthesis gas production devoted to *refinery operations*, *gas to liquid transformations* and *small scale distributed H_2 production*. With this purpose we will initially define some major technological needs and subsequently how short

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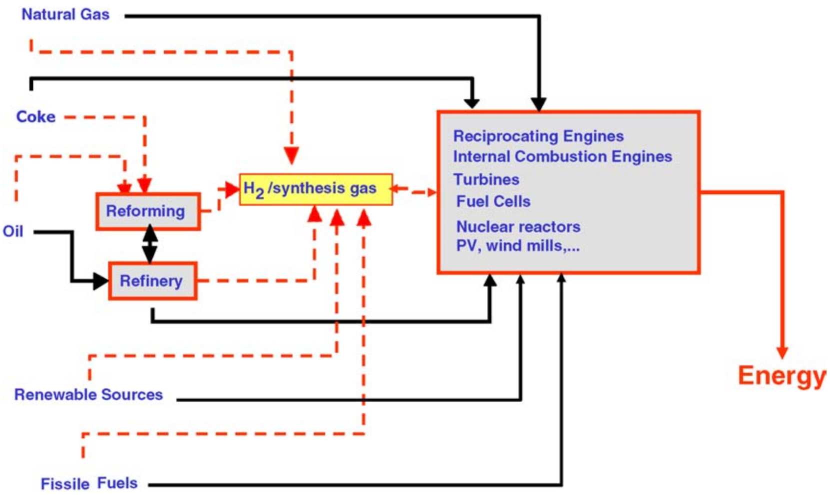

Fig. 1. Parallel energy production chains in which the primary sources are either directly transformed (solid lines) or via-the intermediate formation of H_2 and synthesis gas (dotted lines).

contact time–catalytic partial oxidation (SCT–CPO) technologies could be developed for contributing to their satisfaction.

2. Hydrogen issues in refinery applications

Indeed refineries are large H_2 consuming environments [4] and this consumption is increasing for enhancing the residue conversion capacity and contemporaneously for producing ‘‘clean burning’’ gasoline and diesel fuels containing very low S amounts and with a reduced aromatic and olefin content.

Some H_2 is sourced inside the refinery fences from catalytic reforming of naphtha that produces most of the aromatics included in the gasoline pool [5]. Some other is recovered from minor off-gas streams. However, the growth of the refineries hydroprocessing capacity, that has raised more rapidly than crude capacity, has largely outpaced the by-product and off-gas H_2 sources and the ‘‘H_2 balance’’ has been achieved through on-purpose production.

Table 1
Simplified reaction scheme occurring in the synthesis gas production processes

		ΔH°_{298K} (kJ/mol)
Steam–CO_2 reforming		
$CH_4 + H_2O = CO + 3H_2$	(1)	206
$CO + H_2O = CO_2 + H_2$	(2)	−41
$CH_4 + CO_2 = 2CO + 2H_2$	(3)	247
Non-catalytic partial oxidation		
$CH_4 + \frac{3}{2}O_2 = CO + 2H_2$	(4)	−520
$CO + H_2O = CO_2 + H_2$	(5)	−41
Autothermal reforming (ATR)		
$CH_4 + \frac{3}{2}O_2 = CO + 2H_2$	(4)	−520
$CH_4 + H_2O = CO + 3H_2$	(1)	206
$CO + H_2O = CO_2 + H_2$	(5)	−41
Catalytic partial oxidation		
$CH_4 + \frac{1}{2}O_2 = CO + H_2$	(6)	−38
$CO + H_2O = CO_2 + H_2$	(5)	−41

Indeed the worldwide on-purpose H_2 capacity has increased 70% between 1995 and 2003. Ninety-six percent of this on-purpose H_2 is produced by steam reforming (SR) (76% from NG, 20% from light naphtha) while partial oxidation (PO) of residues (petroleum coke, deasphalter pitch, residual oil) produces the remaining 4%.

The SR and PO characteristics have been extensively reviewed in the literature [6,7] and their main reactions are included in Table 1.

SR is an energy efficient [8] and reliable technology. The H_2 is produced from desulphurised and light hydrocarbons through highly endothermic reactions. The reaction heat is provided by a furnace system including tubular reactors filled with Ni based catalysts. The larger SR furnaces can contain more that 600 tubes (each with a diameter of 100–150 mm and a length of 10–13 m) and can produce a synthesis gas stream sufficient for recovering more than 250,000 Nm^3/h of H_2 [9].

The non-catalytic PO is an alternative to SR. However, as already mentioned, it has still a minor utilisation for refinery on-purpose H_2 production. The process is based on very exothermic reactions produced inside a combustion chamber. The reaction scheme reported in Table 1 largely oversimplifies the complex homogeneus phase radical chemistry occurring in PO reactors.

PO has a unique flexibility with respect to the possibility of utilising various feedstock ranging from NG to deasphalter pitch and to petroleum coke. Its relatively low diffusion is related to the high capital costs (that can double those of a SR of analogous capacity) and to the oxygen consumption features making its economics competitive with those of SR only for large-scale applications ($F_{H_2} > 250,000\ Nm^3/h$).

However, the diffusion of PO is expected to increase due to the falling demand of heavy residues and to the possibility of realising very large plants producing H_2 for the refinery and synthesis gas for IGCC.

A weak point common to both SR and PO concerns their relatively low flexibility with respect the variation of the production capacity [10].

These and other consideration indicated the opportunity of pursuing a R&D effort for developing a catalytic technology with characteristics intermediate to SR and PO having a higher flexibility with respect to the feedstock composition than SR and requiring much lower capital costs than PO and having moreover, a high flexibility with respect to the H_2 production capacity.

3. Synthesis gas issues in GTL applications

The economics of GTL are different from those of oil refining. In a refinery the cost of the raw materials dominates while the capital costs are responsible of a relatively small part of the production costs. The capital costs have instead a major impact with respect to raw materials costs, in determining the economics of the GTL processes [11]. These comprise three major sections represented in Fig. 2. The first section includes the production of synthesis gas. The second is constituted by the synthesis of the liquid fuels (gasoils, gasoline, naphtha, waxes, MeOH/DME). The third concern a final product upgrading, separation and purification.

The synthesis gas preparation is roughly responsible for about 60–70% of the total cost of GTL. The liquid fuel production cost corresponds to the 20–25% and the final product upgrading and purification absorbs the remaining 5–15%. This cost splitting depends both on the intrinsic characteristics of the single processes but also on their integration strategy.

The optimum synthesis gas composition required for the synthesis of the MeOH and DME and for the high-temperature F–T synthesis should satisfy Eq. (7). This occurs because both CO and the CO_2 participate to these chemical processes.

$$M = \frac{H_2 \div CO}{H_2 + CO_2} \cong 2 \tag{7}$$

Instead the CO_2 does not participate in the chemical reactions of the low-temperature F–T processes [2,12]. These are the object of main GTL initiatives for producing naphtha (15–25%, v/v), middle distillates (50–75%, v/v) and lube waxes (0–30%, v/v).

The optimum synthesis gas for the low-temperature F–T process would have H_2/CO ratios slightly higher than 2 (v/v) and a low content of CH_4 and CO_2 (<3%, v/v in the dry synthesis gas).

These synthesis gas characteristics would allow the achievement of the highest overall carbon efficiency, combining high conversion per pass in the F–T reactor with good selectivity towards the desired liquid products.

SR cannot directly produce the synthesis gas for the low-temperature F–T synthesis. PO instead has been utilised in a major first generation low-temperature F–T plants in Bintulu [13]. However, PO needs to be operated at very high temperatures (1300–1400 °C) for obtaining a high methane conversion and for reducing the soot formation [14]. These conditions raise investment and operation cost.

Currently, the preferred synthesis gas production technology is the autothermal reforming (ATR) [15] that can be seen as an hybrid of PO and SR (see equations in Table 1). The ATR utilises a highly desulphurated and pre-reformed NG that is mixed with steam and oxygen and burned in a combustion chamber. Here, the reaction conditions determine peak temperatures lower than those of PO. The partially combusted gas is then flown through a Ni bases catalyst where some of the combustion heat is ''chemically recuperated'' through the occurrence of the endothermic steam–CO_2 reforming reactions. These characteristics allow the avoidance of soot formation reactions the reduction of the oxygen consumption features with respect to PO [16] (Fig. 3).

However, the characteristics that have made ATR the currently preferred technology for GTL applications still leave some margins of improvement.

Indeed, the steam addition, required by ATR for operating under soot-free conditions, raises the H_2/CO ratios in the product synthesis gas well above the desired 2 (v/v) ratios. For this reason major ATR licensors have intensively tried solutions for reducing the steam/carbon (S/C) ratios reaching a S/C limit corresponding to 0.6 (v/v). This value is still too high for obtaining $H_2/CO \approx 2$ (v/v). For this reason some of the CO_2 rich synthesis gas exiting from the

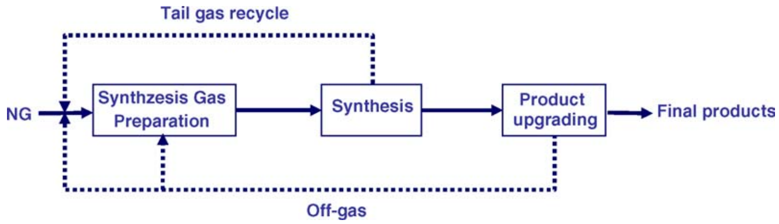

Fig. 2. Simplified GTL scheme including the three main block processes and showing main recycle options to the synthesis gas preparation.

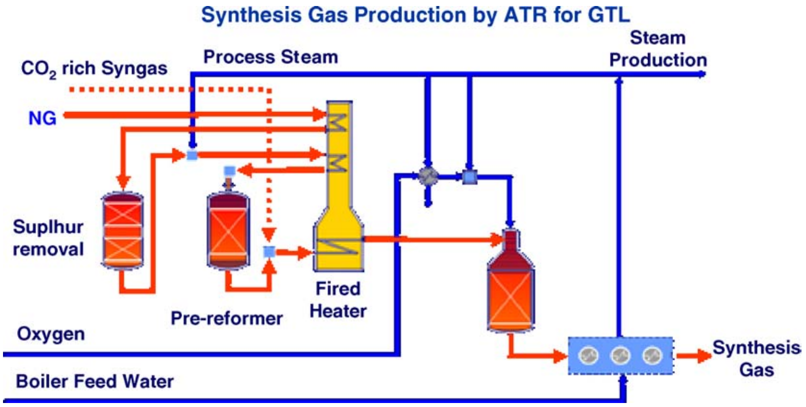

Fig. 3. Simplified process scheme utilising ATR technology for producing synthesis gas for the low-temperature F–T synthesis.

F–T reactor is recycled to ATR, thus enhancing the contribution of the CO_2 reforming and reducing the H_2/CO to the desired value [17]. However, the larger the amount of the CO_2 rich gas recycled, the larger will be the dimensions of the synthesis gas section per tonnes of product and the related investment costs.

In most cases the CO_2 recycle could be avoided operating at $S/C = 0.2$ (v/v), a limit that seems achievable to SCT–CPO of NG. The validation of this technological result is intensively pursued at bench and pilot scale levels.

4. H_2 and synthesis GAS issues in fuel cells and distributed E.E. production

Many fuel cell (FC) systems do exist and their characteristics are widely reviewed and described in the literature [18]. Although public interest in FC remains high, developers are still struggling to overcome technological and economical barriers including limited operating life, high costs and competition with established technologies.

FC convert the chemical energy directly into E.E. and have greater efficiency, less noise and far less pollution than combustion technologies.

The wide interest they have attracted is not only related to their potential environmental benefits but also to the potential changes they could introduce in the traditional ways of producing and distributing E.E.; for instance, introducing a distributed-generation model in which the fuels are transported while the E.E. is originated at the utilisation sites.

The ultimate fuels that FC consume at the anode side are H_2 or synthesis gas.

Even if a great effort has been devoted to develop on board reformers virtually all the fuel cells powered vehicles (520 worldwide at the end of 2004) utilise H_2 that is stored onboard and that can be produced in large centralised facilities or in small and easy to handle reformers localised at the distribution sites.

The most desirable characteristics of these small reformers can be listed as follows: (a) compactness and simplicity, (b) safety and easy operability, (c) low manufacturing cost and (d) multi-fuel capability. We believe that air blown SCT–CPO based technologies could be developed with these characteristics.

5. SCT–CPO characteristics and applications

Initial observation on the occurrence of short contact time hydrocarbon oxidation processes were reported in the scientific literature in the years 1992–1993 [19]. Now it is known that these processes are produced colliding for few milliseconds, gaseous premixed reactant flows with extremely hot catalytic surfaces. These conditions determine a fast and selective chemistry confined inside a thin (<1 μm) solid–gas inter-phase zone surrounding the catalyst particles. Here, the molecules spend 10^{-6} s at temperatures that can be varied between 700 and 1250 °C. Moreover, the processes occur in conditions avoiding the propagation of the reactions into the gas phase that remains relatively at low temperature ($T_{in} < 250\,^{\circ}C$, $T_{out} < 1050\,^{\circ}C$) and chemically cool. These conditions favour the formation of primary reaction products inhibiting chain reactions leading to their degradation.

Indeed the fundamental studies [20,21] indicate that partial oxidation products together with total oxidation products are directly produced through parallel and competing surface reactions and that the formation of partial oxidation products is favoured under SCT conditions due to the very high surface temperatures. These temperatures in some local situations are much higher than those predicted from thermodynamic equilibrium calculations assuming that the reactors are adiabatic. The occurrence of the reactions in these local environments determines in some cases conversion and selectivity values higher than those predicted by the thermodynamic equilibrium at the reactor exit temperatures [22]. Moreover, the very high surface temperatures inhibit catalyst deactivation phenomena related to chemical poison effects.

For these and other related reasons, this chemical process is carried out in very small reactors having a very high flexibility with respect to reactant flow variations. It has also been found that several hydrocarbon reactants including sulphur and aromatic compounds can be treated for producing synthesis gas.

These characteristics are under investigation for developing technologies suitable for: (a) reforming various refinery hydrocarbon streams including those having a high aromatic and sulphur content, such as the cycle oils (LCO) and the high cycle oils (HCO) and the deasphalted oils (DAO), (b) reforming NG at low S/C values till S/C $\cong 0.2$ (v/v) avoiding pre-reforming and pre-heating sections and reaching a synthesis gas composition with $H_2/CO \cong 2$ (v/v) useful for miximising carbon efficiencies, and hence reducing the amount of recycled synthesis gas in low temperature F–T synthesis and (c) realising small and simple air blown SCT–CPO (pre-) reformers for stationary FC or for producing the H_2 inside filling stations devoted to a possible future automotive market.

5.1. H_2 for refineries via SCT–CPO

SCT–CPO plants having a capacity of 10 Nm^3/h of synthesis gas have been operated in our bench-scale facilities reforming NG, refinery off-gases, LCO and DAO. The experiments have been performed at space velocities comprised between 50,000 and 250,000 h^{-1}. The catalysts stability has been tested with lifetime tests successfully prolonged for 500 h when utilising feedstock containing relevant amounts of S and aromatics (the LCO and the DAO contained S 0.5–3.0 wt% and aromatics 70–80 wt%). The examined technical and economic characteristics of the process are appealing. The technology is being scaled-up into a pilot plant unit that is under construction in Milazzo (Sicily). The pilot plant has been designed as a multi-purpose facility for operation with oxygen, enriched air or air and for processing various gaseous and liquid hydrocarbon feedstock. The pilot plant would also include WGS and PSA sections.

Major issues to be addressed concern the definition of safe mixing operation and inlet characteristics avoiding flame ignition.

5.2. SCT–CPO units for low temperature F–T synthesis

A representative process configuration utilising ATR includes: (a) an initial hydrodesulphurisation step, (b) the mixing and heating of the desulphurised NG with steam (reaching a S/C = 0.6, v/v), (c) the pre-reforming of the NG for converting the $C2^+$ hydrocarbons, (d) the mixing of the pre-reformed NG with some of the CO_2 rich synthesis gas produced at the exit of the F–T reactor, and finally (e) the ATR step and the synthesis gas cooling step.

The same front-end process (see Fig. 4) based on the SCT–CPO technology would not utilise the pre-reforming section, would reduce the amount of steam addition allowing operation at S/C = 0.2 (v/v), and would not require the addition of the CO_2 rich stream coming from the F–T recycle loop. Moreover, the reactant gases would enter into the SCT–CPO reactor at temperatures around 250 °C. Such a design would reduce the pre-heating ‘‘duty’’ and consequently the capital cost expenditures for the synthesis. At the same time the avoidance of the recycling of the CO_2 rich synthesis gas would determine a relevant increase of the entire GTL single line capacity [23]. A drawback in the SCT–CPO technology could concern the oxygen consumption that it is expected to be slightly higher than for ATR. However, it is also expected that the relevant reduction of the investment cost of the synthesis gas unit would overcome the slight increase of the cost of the air separation unit.

Despite these advantages it has to be mentioned that the reliability and safety of SCT–CPO would require an extensive demonstration phase. For this reason, we estimate that an extensive testing period would be required before that the final technological and economical potential of large scale SCT–CPO plants could be entirely defined.

The safety issues would be much less relevant if SCT–CPO could be performed utilising air instead of pure oxygen.

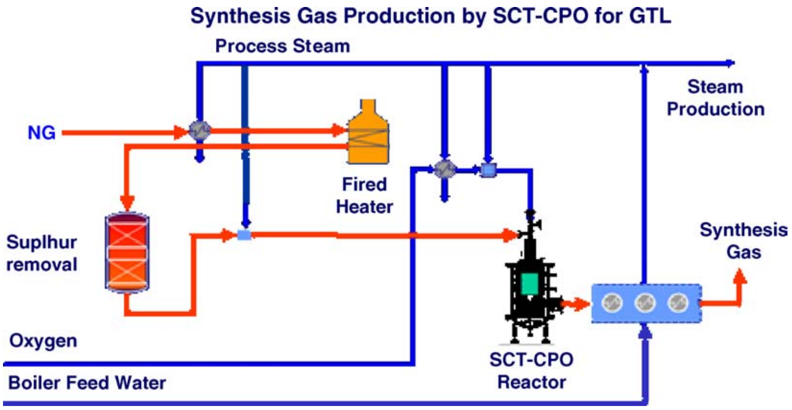

Fig. 4. Simplified process scheme utilising SCT–CPO technology for producing synthesis gas for the low-temperature F–T synthesis.

However, this option would not be economically advantageous in existing large-scale GTL initiatives. Here, the air compression costs and the presence of N_2 in the produced synthesis gas would have a relevant negative impact on the economics.

However, some perspectives, particularly in off-shore application, do exist and in our opinion are mainly linked to the possibility of performing the F–T synthesis with a high conversion per pass with a N_2 containing synthesis gas.

5.3. Air blown SCT–CPO for stationary FC or for producing the H_2 inside filling stations

Small scale reformer solutions have been designed as separate units for feeding stationary FC systems and/or for producing the fuel of H_2 fueled vehicles [24]. Some other solutions have been developed as components of FC systems.

Here, we briefly report on the characteristics of: (a) a small air blown SCT–CPO reformer for producing pure H_2 inside a multi-fuel station and (b) an air blown SCT–CPO pre-reformer for SOFC applications.

Concerning the point (a) it is mentioned that a multi-fuel station would be realised inside the urban area of the Italian city of Mantova for delivering gasoline, diesel, NG and H_2 to internal combustion engines (ICE) and FC vehicles. The project is sustained by the European Union [25] and include twins initiatives in Germany and in Italy. In Mantova the H_2 will be produced through an air blown SCT–CPO reformer designed for being tightly integrated with the multi-fuel station needs and characteristics. This integration would reduce the greenhouse gas emissions and the waste of energy and will demonstrate the possibility of spreading the cost of the stationary H_2 production unit over different applications. The H_2 (50 Nm^3/h) will be produced from NG that will also be distributed to ICE vehicles. The reformer is being designed for fast and easy start-up and shut-down operation required for following a variable H_2 demand.

Concerning point (b) it is mentioned that a SCT–CPO pre-reformer system has been realised and experimented for more than 1000 h in our laboratories in S. Donato Milanese (MI). The pre-reformer has a very simple lay-out suitable for integration with a SOFC system. The reformer has been operated at $O_2/C = 0.1–0.5$ (v/v) without requiring steam addition for avoiding soot formation. These performances would not be possible in SR, ATR or PO systems as already pointed out.

6. Conclusions

Some H_2 and synthesis gas production issues related to: (i) refinery, (ii) GTL and (iii) FC have been examined revealing major technological needs that could be accomplished developing SCT–CPO systems whose main characteristics have been briefly summarised. In particular, it has been reported that the ongoing R&D effort has reached a pilot scale level. The pilot plant has been designed for a multi-purpose utilisation for testing SCT–CPO systems: (a) able to tune the H_2 production capacity with the refinery requirements and allowing the utilisation of several hydrocarbon feedstock (refinery off-gases, NG, naphtha, gasoils, LCO, HCO, DAO, ...), (b) able to operate at S/C values lower that those of ATR, thus permitting to reduce investment and the production capacity of the GTL single train processes and (c) for producing H_2 inside multi-fuel station and pre-reforming NG and liquid fuels for SOFC applications.

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