An overview of novel technologies to valorise coke oven gas surplus

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Abstract

The steelmaking industry is the largest energy consuming manufacturing sector in the world and is responsible for 5-7 % of anthropogenic CO_2 emissions. It is therefore necessary to increase energy efficiency and reduce greenhouse gases emissions in these industries. COG, a by-product of coking plants, is one of the key ways to achieve these goals. COG, which is used as fuel in different processes of the steelmaking plants, is a H_2-rich gas with a high energetic potential. However, there is a significant surplus that usually is burnt away in torches, and even directly emitted into the air. With the aim of tackling this wasting of resources and energy inefficiency, several alternatives have been proposed during recent years. In the present work, these alternatives are reviewed and their main advantages and drawbacks are discussed.

Keywords

Coke oven gas, Hydrogen, Reforming, Synthesis gas, Methanol, Energy recovery

Contents

1. Introduction

The steel industry is the largest energy consuming manufacturing sector worldwide [1,2]. Consequently, their associated CO_2 emissions account for about 5-7 % of the total anthropogenic carbon dioxide emissions [1,2]. Taking into account that steel production is expected to increase during the next few decades, a significant increase in energy consumption as well as CO_2 emissions are also expected to follow [1-3]. The steel industry has been committed to sustainability since 1960's, and in some countries (e.g. France) these have reduced CO_2 emissions and energy consumption by 60% and 50%, respectively, per tonne of steel produced [1]. However, manufacturing processes of the steel industry have reached high levels of efficiency and are very close to their physical limits in terms of carbon use [1]. Energy and greenhouse gases (GHG) emissions concerns have created the need to seek for alternative ways to improve the energey efficiency of steel plants decreasing (if possible) at the same time carbon dioxide emissions [1,2,4-6]. An interesting example of initiatives related to this concern in the iron and steel industry is the program COURSE50 ("CO2 Ultimate Reduction in the Steelmaking Process by Innovative Technologies for Cool Earth 50"). This program is currently being developed in Japan to find alternative uses for blast furnaces and coke oven gases in order to reduce carbon dioxide emissions and improve energy efficiency in Japanese steel industries [6].

Coke oven gas (COG) is a point of high interest to enhance energy efficiency and reduce GHG emissions in the steel industry [2,3,5,6]. COG is a by-product of coal carbonisation to coke which is co-generated in the coking process [7]. In spite of the reduction of coke consumption in the blast furnace (and therefore COG production), during the past few decades, blast furnaces cannot operate without coke which implies COG will continue to be produced in large quantities in the future [3].

COG, has a very complex composition after leaving the coke oven. Firstly, the gas is cooled down to separate tars to subsequently undergo different scrubbing processes to eliminate NH_3, H_2S and BTX [3]. After these conditioning stages, cold COG comprises H_2 (~55-60 %), CH_4 (~23-27 %), CO (~5-8 %), N_2 (~3-6 %), CO_2 (less than 2 %) along with other hydrocarbons in small proportions. Currently 20-40 % of COG produced is normally utilised as fuel in the actual coke ovens [8-10]. The remaining COG generated

is generally employed in alternative processes of the steel mills [3,7] but most surplus is currently burnt off in torches and even in some cases directly emitted to the air [10,11]. These vary due to the highly dynamic nature of the steel-making process [8].

In addition, COG approximately accounts for 18 % of the energy output of a coking plant due to its large low calorific value, which varies from 17 to 18 MJ/m^3 [3]. Both COG energetic properties and production excess lead to large GHG emissions, energy inefficiency and most importantly a significant environmental impact which in turn is also reflected in a clearly improvable economic efficiency [3,4,12]. As an example of this inefficiency, U.S. Steel Corp. has been able to save over 6 million dollars annually by using COG as fuel in blast furnaces [8].

During past few decades, various alternatives to valorise COG have been proposed, including its use for energy production, a direct utilisation in the blast furnace to produce "pig iron" or gas treatment for the production of chemicals and fuels.

This work is aimed to provide an overview of some of the most promising and challenging technologies from the research viewpoint. Proposed alternatives can be grouped into three main categories: hydrogen separation, synthesis gas production and other technologies.

Each of these alternatives requires different preconditioning stages as the presence of some COG components (especially H_2S and NH_3) may be highly damaging for the processes [3,4,13]. This will be described in detailed in each section.

2. Hydrogen Separation

Hydrogen is the main and most valuable component in COG, which is the reason why COG has been proposed as an alternative hydrogen source. Pressure swing adsorption and membrane separation have been the two main technologies proposed for this purpose, although other possibilities have also been investigated including hydrate formation and cryogenic separation.

2.1. Pressure swing adsorption

The leading technology to efficiently separate hydrogen from COG is pressure swing adsorption (PSA) [6,7,11,14-23]. This technology is a low-cost, low-energy and highly efficient gas separation process [24]. PSA processes employ several parallel units that operate in consecutive steps. Figure 1 shows a schematic representation of the operating steps in a system comprising two adsorption beds. The process commences with an adsorption step, in which the crude gas flows through a PSA unit filled with adsorbent materials at the highest operation pressure. The adsorbable substances are retained by the adsorbents and the rest of the gas leaves the unit. After a period of time, the adsorbent saturates and the operation is stopped. At this point, the adsorbent needs to be regenerated at the lowest pressure, so the unit needs to be depressurised. The depressurisation cycle is terminated by counter-flow expansion down to the lowest pressure, called dump step. The adsorber is regenerated with a gas stream which purges all the adsorbed impurities. Finally, the adsorber is brought back to high pressure conditions to resume adsorption. These cycles operate at constant temperature, requiring no heating or cooling steps [24,25]. Different adsorbent materials are utilised for hydrogen recovery, most commonly carbonaceous materials, alumina oxides or zeolites [16, 17, 19, 24].

Other components in COG (e.g. higher hydrocarbons, H_2S or NH_3) have to be removed before reaching the adsorption bed owing to issues associated to bed saturation (as they cannot be desorbed by decreasing the pressure in the systems) [3,18]. For this reason, COG needs to undergo complete preconditioning prior to its utilisation in PSA processes.

Two different streams, namely a H_2-rich stream and a highly concentrated CH_4 gas, are generally obtained in PSA H_2 separation from COG. The methane-enriched stream can be considered as a substitute of natural gas (SNG), with the possibility to be employed as fuel in various plant processes in a similar way to COG. However, the loss of energetic power due to H_2 separation from COG needs to be compensated by other fuels if this methane-rich stream is used as fuel [7,15,16]. Other technologies should be obviously used in combination with PSA to achieve an optimum valorisation of COG.
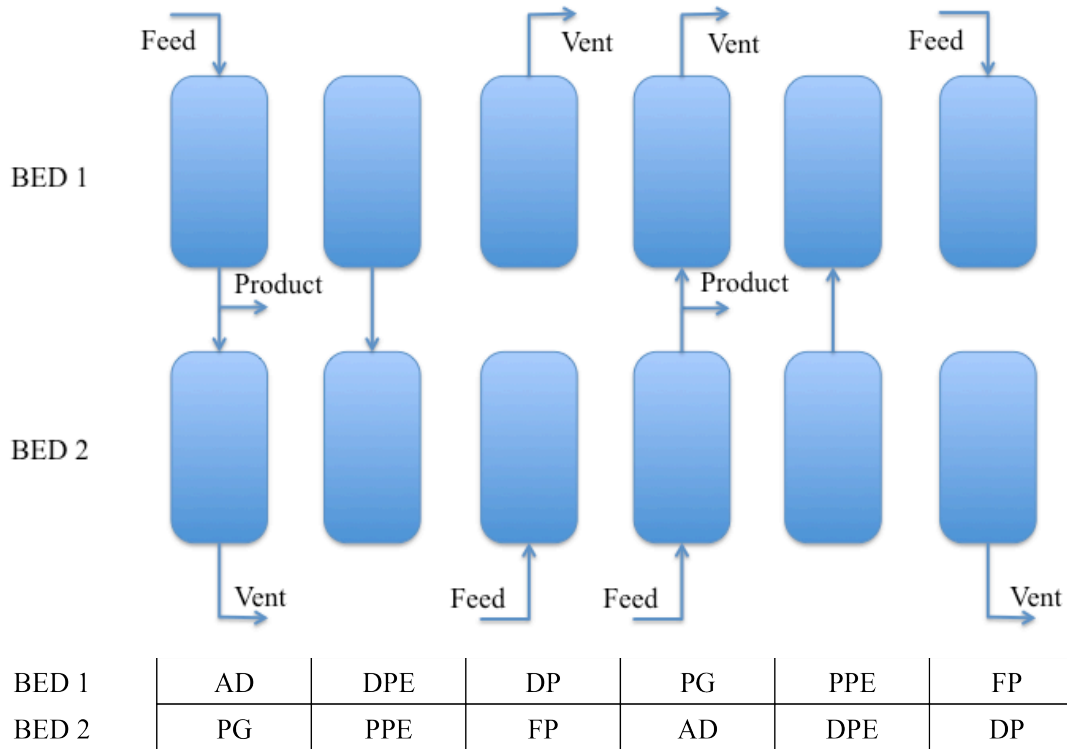
BED 1	AD	DPE	DP	PG	PPE	FP
BED 2	PG	PPE	FP	AD	DPE	DP

Fig. 1. Scheme of the operation steps of a pressure swing adsorption system composed of two adsorption beds (AD, adsorption; DPE, depressurizing pressure equalization; DP, depressurization; PG, purge; PPE, depressurizing pressure equalization; FP, feed pressurization). Adapted from [20]

Most studies published in the field of PSA have considered simple mixtures with two or three components, which cannot possibly have a similar behaviour to that of COG [18,19]. Yang and Lee [18] studied the dynamics of the system and proposed a mathematical model of PSA adsorption to recover H_2 from COG using a layered bed of activated carbon and zeolites. These authors claimed that the composition of the bed is a key parameter in the process, since the employed materials can influence the concentration of the major impurity in the final stream. In the particular case of a layered bed of activated carbon and zeolites, it is necessary to establish the optimum carbon ratio (defined as the ratio of activated carbon layer length to the bed length) [18,21]. Another interesting conclusion of these studies is that, although N_2 is a minor impurity in COG, it can play an important role in the process, giving rise to different breakthrough times for the rest of the components fed into the PSA column [21,22]. Ahn *et al.* [20] included a backfill step in the PSA process and found that this additional

step increased H_2 purity in the final stream at the expense of decreasing H_2 recovery. However, H_2 purities higher than 99.99 % were very difficult to achieve.

Further studies beyond fundamental research have also been conducted to ascertain a plausible implementation of this technology at industrial level. Joseck *et al.* [7] explored the possibility of H_2/COG separation by means of PSA technology, aiming to valorise COG for fuel cell vehicles (FCVs). The study was carried out in the Rust Belt (Midwest-Northeast US area with an important network of coking and steel plants) and showed that H_2 obtained from such a large concentration of plants could fuel ca. 1.7 million FCVs. The economics of the project however need to be thoroughly examined but the project can in principle offer a significant potential in terms of energy savings and reduction of GHG emissions.. A similar study conducted by Hwang and Chang [23] assessed the possibility to use hydrogen from different sources in fuel cell scooters in Taiwan. Life-cycle Analysis studies revealed that FC scooters fueled with hydrogen from COG accounted for the most efficient technology, resulting in remarkably reduced GHG emissions together with a improved energy efficiencies.

2.2. Membrane separation

Another recently proposed technology for hydrogen recovery from COG is membrane separation [11]. Membrane gas separation is a pressure-driven process which entails several advantages compared to other technologies (i.e. easy operation, low capital and operating costs and low-energy requirements) [26]. In a membrane separation process, a gaseous mixture at high pressure is forced to pass through the surface of a membrane which is selectively permeable to one or more of the gas components. As a result, the permeate (stream obtained after it has passed through the membrane) can be enriched in these components while the retentate (stream that does not pass through the membrane) is therefore enriched in the rest of the components. A basic scheme of the process is shown in Figure 2 [25,27]. Shen *et al*. reported that a H_2-rich stream (>95% maximum H_2 concentration)and a CH_4-rich stream (70% maximum CH_4 concentration) could both be obtained using an organic membrane [11]. However, membrane technologies have been mostly applied in the form of membrane reactors for to syngas production processes, to increase conversions and selectivities, as detailed in Section 3.
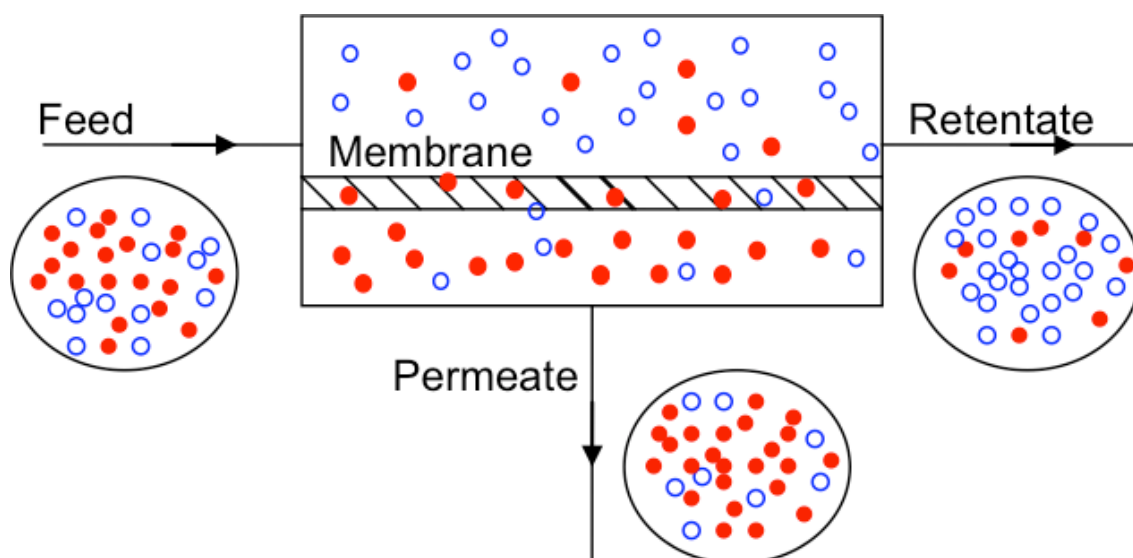
Fig. 2. Scheme of the operation of a separation membrane system

2.3. Other technologies

Other hydrogen separation technologies including cryogenic separation [28] and hydrate formation [29] have been proposed as alternatives to PSA and membrane separation for COG valorisation. Cryogenic separation processes proposed by Chang *et al.* [28] comprising four steps, namely 1) separation of heavier compounds (hydrocarbons like ethylene and propane) 2) methane separation 3) O_2-CO-N_2 separation and 4) eventual separation-liquefaction of hydrogen. While the principles of the proposed methodology are sound, this technology is still in its infancy and needs to undergo further developments and studies prior to a potential implementation at industrial scale.

Comparatively, hydrate separation has the advantage of being a simple process which can be operated at mild conditions. Hydrates are non-stoichiometric crystalline compounds formed by small molecules of gas and water under certain temperature and pressure conditions [29,30]. A maximum H_2 concentration of 80 vol. % in the final product has been obtained using this hydrate methodology, with recovering yields in the 72-90% range [29]. Apart from a low hydrogen concentration, the technology has associated drawbacks including the need to use additives such as tetrahydrofuran (to decrease pressure operation) or sodium dodecyl sulfate (to increase reaction rates). The proposed technology has promising prospects of application in hydrogen recovery from

COG but it is currently at a very low stage of development compared to alternative available technologies.

3. Synthesis gas production

Synthesis gas (syngas) is a H_2 and CO enriched mixture utilised as raw material for the large scale production of hydrogen and a wide variety of organic products and fuels [31]. Syngas has been extensively produced from natural gas and oil, but the limited supply of fossil fuels and concerns on climate change and GHG emissions have intensified the search for alternative processes of syngas production including biomass gasification [32], biogas reforming [33] and the thermal upgrading of COG [5,9,10,34-55]. The main thermal upgrading technologies studied for COG valorisation include steam [34-39,43-45,49] and dry reforming [9,40-42,46-48] as well as partial oxidation [10, 50-55]. Turpeinen et al. [56] reported an interesting thermodynamic analysis of COG conversion into hydrogen using these three different technologies as compared to other potential hydrogen sources (e.g. natural gas, biogas and refinery gas). This study conveys an idea of the remarkable potential of COG as a source of syngas, particularly related to the use of the produced syngas for hydrogen generation. COG is clearly the best source in terms of energy consumption and CO2 emissions when steam and especially dry reforming is conducted. Partial oxidation of COG still gives rise to the lowest CO_2 emissions but syngas production from natural and refinery gas is less energy consuming [56].

All proposed methodologies employ a catalyst which can be severely poisoned by the presence of some COG components. For this reason, a cleaning process (e.g. scrubbers or absorbers) is required prior to reaction [3, 57, 58]. In the case of dry reforming, the development of the SPARG process (where the catalyst is partially poisoned with H_2S to avoid coke formation) may avoid the need to remove H_2S [59, 60].

3.1. Steam reforming

The steam reforming of methane (Reaction 1) is currently the main process for hydrogen or syngas production. This process involves the heterogeneously catalysed reaction of methane and steam to obtain a syngas with high H_2/CO ratio (theoretically

3/1). Nearly all metals from Group VIII have been investigated as supported on various supports. Ni has attracted most interest due to its greater availability and lower cost compared to the other metals. Normally, the reaction takes places in tubular reactors, the catalyst being placed inside the tubes. The process is carried out at high temperatures (700-1000 ºC) as the steam reforming of methane is a highly endothermic reaction. The pressure is normally mild (20-30 bar), although the reaction produces an increase in the net number of moles and, therefore, high pressures lead to a reduction in the conversion of the systems. This is assumed because the products are normally used in processes at high pressure and it is cheaper to compress the methane and the steam than the synthesis gas produced. Moreover, carrying out the process under pressure allows smaller reactors to be used [57,61-63].

$$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO \hspace{4cm} \text{(Reaction 1)}$$

Side reactions may take place between the different species present in COG. This may affect the selectivity of the process and the final product composition. Some examples of side reactions include water gas shift (WGS), reverse WGS chemistries (Reaction 2) and dry reforming processes (Reaction 3), as well as CH_4 decomposition (Reaction 4) and the Boudouard equilibrium (Reaction 5).

$$H_2O + CO \leftrightarrow H_2 + CO_2 \hspace{4cm} \text{(Reaction 2)}$$

$$CH_4 + CO_2 \leftrightarrow 2\ H_2 + 2\ CO \hspace{3.5cm} \text{(Reaction 3)}$$

$$CH_4 \rightarrow 2\ H_2 + C \hspace{4.5cm} \text{(Reaction 4)}$$

$$C + CO_2 \leftrightarrow 2\ CO \hspace{4.5cm} \text{(Reaction 5)}$$

One of the most critical factors in the steam reforming of methane is H_2O/CH_4 ratio. Steam is generally injected in excess over the stoichiometric value of the reaction ($H_2O/CH_4>1$) as it prevents catalyst deactivation caused by carbon deposits on the catalyst [57,61]. Excess steam is used to prevent the formation of coke, while additional heat is needed, so a lower H_2O/CH_4 ratio is desired to improve the energy efficiency of

the process. In the case of the steam reforming of COG, this ratio may differ from that used in the steam reforming of methane, as the presence of H_2, CO_2 and CO in COG influences the equilibriums of the different reactions involved in the process. Zhang *et al*. [38,45] reported that the thermodynamically permissible H_2O/CH_4 value should be in 1.1-1.3 range, at temperatures between 950-1000ºC. A kinetic model for the steam reforming of COG was also proposed taking into consideration the combination of steam and dry reforming (due to the presence of carbon dioxide in COG). Results revealed that both reactions were of first order from methane, steam and carbon dioxide, with kinetic parameters shown in Table 1. Changing the H_2O/CH_4 ratio to 1.0 was also found to be possible using a NiO/MgO catalyst due to excellent coking resistance of the catalyst [43].

Table 1. Kinetic parameters of the steam reforming of COG [38]

	A	E_a (J/mol)
Steam reforming rate (K_{SR})	$4.56 \cdot 10^9$	21373.4
Dry reforming rate (K_{DR})	$8.06 \cdot 10^8$	20843.7
Kinetic equation	$r_{CH_4} = A_{SR} \cdot \exp\left(-\dfrac{E_{a\ SR}}{T}\right) \cdot C_{CH_4} \cdot C_{H_2O} + A_{DR} \cdot \exp\left(-\dfrac{E_{a\ DR}}{T}\right) \cdot C_{CH_4} \cdot C_{CO_2}$	

The use of hot COG (no conditioning processes prior to leaving the coke oven) in the steam reforming process has been widely proposed to reform methane as well as the tarry components, taking advantage of the high temperatures of the gas to promote the desired reactions [34-37,39,44,49]. As hot COG contains ca. 10-15% steam, the energy efficiency and cost of the process can be improved as lower quantities of steam need to be injected in the system. Tars usually account for 30 wt% of hot COG, the main components being naphthalene, benzene, pyrene and toluene [34,35]. These species compete with each other and with methane in steam reforming processes, especially naphthalene (the only component which reacts at temperatures below 750 ºC while at higher temperatures the other compounds react once naphthalene has been completely converted) [34]. Steam reforming of hot COG can be carried out in the presence or

absence of catalysts, but the presence of a catalyst significantly improves the results obtained. The main disadvantage of using hot COG is related to the lower ratio H/C obtained as compared to conditioned COG which in turn leads to a very important production of carbonaceous deposits of different nature in the system (i.e. well-ordered graphite, non-oriented carbon forms, carbon filaments and metal carbides) depending on the working temperatures [49]. The generation of carbonaceous deposits also increases the deactivation rate of the catalyst. The presence of hydrogen, an adequate load of active metal as well as an appropriate steam/carbon ratio could contribute to reduce such deactivation rate [39,44,49]. The presence of H_2S is also highly undesirable due to its poisoning effects on catalysts (e.g. Ni) but generally this deactivation effect is low and the catalyst can easily be regenerated [34,49]. Remarkably, this technology can potentially generate 3-5 times more H_2 to that of the COG before undergoing the reforming process, making the steam reforming of hot COG one of the most promising alternatives for H_2 production from COG. Reports may indicate that hydrogen can be produced by combining steam reforming and partial oxidation of hot COG, reducing by 30% production costs as compared to PSA mediated direct hydrogen separation from the COG [37].

3.2. Dry reforming

CO_2 reforming or dry reforming of methane (Reaction 3) has been widely proposed as an alternative process to steam reforming of methane [64-68]. The increasing interest in this process is based on the lower energy requirements compared to steam reforming together with the consumption of two commonly extended greenhouse gases such as CH_4 and CO_2, with an eventual generation of highly valuable products. CO_2 reforming also allows the production of a low H_2/CO ratio syngas (theoretically 1/1, although the presence of side reactions, such as reverse WGS slightly reduces it), which is suitable for the production of higher hydrocarbons and oxygenated derivatives [31,66].

$$CH_4 + CO_2 \leftrightarrow 2\,H_2 + 2\,CO \qquad \qquad \text{(reaction 3)}$$

As in the case of steam reforming, dry reforming must be carried out in the presence of a catalyst. Once again, Ni has been the most commonly metal utilised as catalyst in dry reforming chemistries, but the drawback to this process is the intense formation of

carbonaceous deposits which leads to a rapid catalyst deactivation. This drawback should be addressed prior to technology implementation at industrial scale. Consequently research efforts related to dry reforming of methane have been focused on the development of commercial catalysts able to achieve high and stable conversions, being at the same time resistant to deactivation [64,65,69-71]. To date, only two processes based on methane dry reforming have been industrially implemented: the SPARG process [59,60] and the CALCOR process for CO production [72].

The SPARG process could be especially interesting in the application of dry reforming methodologies to COG. This technology is based on the addition of H_2S to the process stream which leads to a partial poisoning of the catalyst but prevents at the same time the formation of carbonaceous deposits in the active centers of the catalyst, keeping high conversions of CH_4 and CO_2 in the systems [59,60]. In this way, the previous scrubbing step required to remove H_2S from COG can be eliminated in the conditioning stages, improving the economics of COG valorisation.
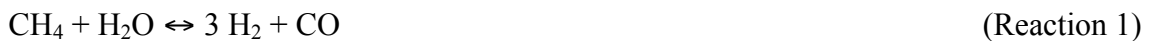
Until now, the application of dry reforming to COG has received less attention than steam reforming or partial oxidation [9,40-42,46-48]. Nevertheless, results reported in these works are encouraging, pointing to a potentially optimum way to transform COG into syngas with a close to optimum $H_2/CO= 2$ ratio to be employed in Fischer-Tropsch (FT) synthesis of chemicals as well as in methanol production. Comparatively, steam reforming of COG gives rise to H_2/CO ratios that are considerably higher than 3 (ratio obtained with methane) [47]. In the case of partial oxidation, the H_2/CO ratio obtained with methane is ca. 2, so that an expected H_2/CO ratio of 2.5-3 will be likely to be the case in COG partial oxidation due to its hydrogen content. These values are not close to the optimal requirements for FT processes and methanol synthesis [47] and entail the addition of further conditioning stages which are not required in the case of dry reforming of COG [9,40-42,47].

Side reactions may also influence the theoretical results in COG dry reforming as observed in other processes. In this case, the reverse WGS (reaction 2) is the most critical. acting as a step in the process, rather than as a side reaction [40], leading to two different alternative pathways:

1. *Direct dry reforming*: methane is decomposed into hydrogen and carbon through reaction 4 and then carbon is gasified to CO through the Boudouard equilibrium (reaction 5).

$$CH_4 \rightarrow 2\ H_2 + C \hspace{4cm} \text{(Reaction 4)}$$

$$C + CO_2 \leftrightarrow 2\ CO \hspace{4cm} \text{(Reaction 5)}$$
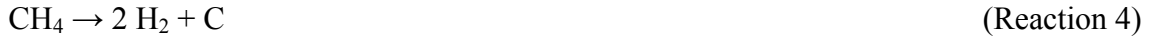
2. *Reverse WGS followed by steam reforming (SR)*: the large amount of hydrogen contained in COG promotes the RWGS reaction (reaction 2), producing water which subsequently reacts with methane (steam reforming) to generate CO and H_2 (reaction 1).

$$H_2 + CO_2 \leftrightarrow H_2O + CO \hspace{4cm} \text{(Reaction 2)}$$

$$CH_4 + H_2O \leftrightarrow 3\ H_2 + CO \hspace{4cm} \text{(Reaction 1)}$$

The direct dry reforming generates carbon as by-product as CO_2 is not generally able to convert all carbon produced to CO, resulting in the deactivation of the catalyst [9,41,47]. Comparatively, the RWGS+SR pathway generates water as by-product which influences H_2 selectivity (reduced) and consequently H_2/CO ratios differ from 2 [9,40-42,47].

Three different types of catalysts have been studied for dry reforming processes. These include carbonaceous materials, Ni supported catalysts and mixtures of both catalysts. Table 2 summarises the best conversion and selectivity results obtained for the different literature reported catalysts.

The most interesting results have been obtained with mixtures of activated carbon and Ni/Al_2O_3 catalysts, since these have been reported to have a synergetic effect [40], which was previously observed in the dry reforming of methane [73]. Interestingly, this synergism that leads to higher activities and selectivities was more noticeable in COG dry reforming [40], with catalysts also being more stable (in terms of BET surface area

reduction) and generating less water [40]. CO was found to have a negative influence on such synergetic effect, pointing out that these catalysts will be more efficient in processing COG of low CO content.

Table 2. Conversions and selectivities of the catalysts studied in the dry reforming of COG.

Catalyst	Temperature (ºC)	VHSV (L/g·h)	Conversions (%)		Selectivity (%)	Ref.
			CH_4	CO_2		
Charcoal	1000	7.5	70	90	n.d.	[48]
Activated carbon	1000	0.75	82	95	90-100	[42]
Ni/SiO$_2$	800	30	75	80	100	[9]
Ni/Al$_2$O$_3$	900	9	90	95	94	[41]
Ni/Al$_2$O$_3$ (67%) Activated Carbon (33%)	800	3,75	85	93	85	[40]

3.3. Partial Oxidation

The partial oxidation of methane (Reaction 6) is a mildly exothermic reaction which yields a syngas with an intermediate H_2/CO ratio between those obtained with steam and dry reforming [74].

$$CH_4 + \tfrac{1}{2} O_2 \leftrightarrow 2 H_2 + CO \qquad \text{(reaction 6)}$$

In this case, side reactions (Reactions 7 and 8) may also affect the process, changing the H_2/CO ratio and reducing its selectivity and efficiency [75].

$$CH_4 + 2 O_2 \leftrightarrow 2 H_2O + CO_2 \qquad \text{(reaction 7)}$$

$$CH_4 + O_2 \leftrightarrow 2 H_2 + CO_2 \qquad \text{(reaction 8)}$$

The partial oxidation of methane can be carried out in two different ways: non catalytic and catalytic [76]. The non-catalytic method is an established industrial process which

operates at high temperatures (>1100 ºC) and mild pressures (50-70 atm, mainly due to the high pressure downstream process, as in the case of steam reforming) and which requires very complex equipment. This normally makes the process even less energy efficient to that of methane steam reforming [62, 74, 76, 77].

The catalytic method has a long history (like steam reforming) but has attracted significantly less attention until the past decade. However, its importance will most probably increase during the next few years due to several advantages [76, 77]:

- It is a mildly exothermic process. This will increase the energetic efficiency of the process in addition to the lower operating temperatures needed due to the use of catalyst (750-1000ºC),. This is probably the most important advantage of the partial oxidation of methane.
- The final H_2/CO ratio is generally 2, that required for methanol production and FT processes. However, this advantage disappears in COG valorisation practises if hydrogen contained in COG is not previously removed (otherwise, the final H_2/CO ratio will exceed 2, making it less suitable than in the case of the dry reforming for the synthesis of chemicals such us methanol or dimethyl ether [9]).
- Product gases have a very low CO_2 concentration, which often needs to be removed prior to the use of syngas in downstream processes.
- Reaction rates are higher compared to those of steam or dry reforming under otherwise identical operating conditions, giving rise to a faster process..

Most research efforts in the field of partial oxidation have been focused on the development of appropriate catalysts for the process, that overcome drawbacks including carbon deposition or loss of active compound during the reaction [75, 77]. Three main types of catalysts have been proposed based on transition metals (nickel, cobalt and iron), and noble metal supported catalysts as well as transition metal carbide catalysts [75, 77]. Due to their lower price and wider availability, Ni, Co and Fe, have been the focus of most studies in spite of the improved resistance to deactivation of noble metal supported catalysts. Nickel has been reported to be highly active and selective for syngas production, but it also efficiently catalyses carbon formation. The use of this particular type of catalyst requires O2 excess working conditions to work

with an excess of O2 to reduce carbon formation. Modification of the support has been reported to improve the stability of the catalyst, but its deactivation is unavoidable with time due to a reduction in the surface area of nickel and carbon deposition. The addition of Co and Fe has been reported to enhance the resistance of the catalyst to deactivation. Iron addition stabilises nickel, as compared to a reduction in carbon formation strongly promoted by cobalt addition (which makes possible to work at lower temperatures in Co-promoted catalysts) [77].

Reports focusing on the application of partial oxidation to COG have been mostly catalytic [10, 50, 51, 53, 78, 79], with only a few reports on non catalysed partial oxidation [54, 55], mostly related to numerical simulations. Chen *et al.* [80] performed a theoretic thermodynamic analysis of the partial oxidation of cold preconditioned COG to study the influence of two critical parameters on conversions and yields: temperature (studied in the interval from 500 to 1750 ºC) and O_2/CH_4 molar ratio (studied in the interval from 0.25 to 1). They also studied the possibility of adding an additional step to the process, a WGS reaction of syngas, aiming to increase H_2 yield. The optimal operating conditions found comprised an O_2/CH_4 molar ratio of 0.5 and temperatures higher than 1000 ºC. Under these conditions, carbon deposition was negligible [80]. A related thermodynamic study reached almost the same conclusions, (namely an ideal O_2/CH_4 molar ratio in the range of 0.46-0.47), but suggested temperatures could be reduced to 800-900ºC for a carbon deposition-free process [81].

A deep analysis of the influence of different reaction conditions on the final syngas produced using Ni/SiO_2 catalysts indicated that oxygen was completely consumed at temperatures from 600 to 900 ºC, and H_2 and CO selectivities increased (H_2/CO ratio decreased) at increased temperatures [9]. This behavior was claimed to be influenced by methane combustion at low temperatures, whereas partial oxidation processes prevailed at high temperatures. The influence of O_2/CH_4 ratio was also studied and shown to be of critical importance in the process [80]. Conversion increased dramatically when O_2/CH_4 ratio was increased from 0.125 to 1.0 at a temperature of 750 ºC. Selectivities to H_2 and CO decreased at O_2/CH_4 ratios higher than 0.5. The authors suggested that these results were a consequence of the consumption of the surplus of oxygen in the complete oxidation of methane (reaction 8) and/or the complete oxidation of the produced H_2 and CO (reactions 9 and 10):

$$H_2 + \tfrac{1}{2} O2 \leftrightarrow H_2O \qquad\qquad\qquad\qquad\qquad \text{(reaction 9)}$$

$$CO + \tfrac{1}{2} O_2 \leftrightarrow CO_2 \qquad\qquad\qquad\qquad\qquad \text{(reaction 10)}$$
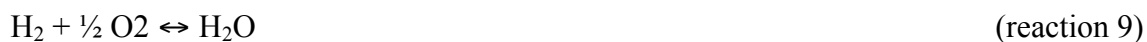
An increase in space velocity favoured the combustion of methane in detriment to partial oxidation. Therefore, the value of the space velocity was suggested to play an important role in order to be able to treat as much gas as possible while avoiding high rates of methane combustion, which will lead to a lower selectivity.

One of the most important issues in the industrial implementation of partial oxidation technologies relates to its elevated cost (in both economic and energetic terms) to supply pure oxygen to carry out the reaction. In fact, as much as 40% of the expenses of a partial oxidation plant come from oxygen production processes [82]. To overcome this problem, the use of membrane reactors has become an attractive alternative to conventional technologies. In the particular case of COG partial oxidation, membrane reactors have been pretty much the only technology to be investigated in recent years [10, 39, 50, 51, 53, 78, 79, 81, 83]. These reactors offer the possibility to feed air directly instead of the need for previous separation processes to feed pure oxygen. Inside the reactor, an oxygen permeable membrane exclusively allows oxygen to reach the catalyst, but not the other components present in the air. A scheme of this system is shown in Figure 3. This technology has shown promising results to date, with yields, conversions and selectivities being as high as those reported using the conventional technology. It can therefore be considered as a potential future alternative for syngas production from COG valorisation [10, 78, 81, 83]. The presence of other species different from methane influences the performance of the membrane in terms of stability and oxygen flux. Hydrogen is a particularly interesting compound which behaves as a "pseudo-catalyst" and favours the oxygen permeation through the membrane when BCFNO membranes (composed of Ba, Co, Fe, Nb and O) are employed [84]. These membranes also show excellent long-term stability. In the light of these premises, research into this type of membrane technologies and reactors for the partial oxidation of COG are likely to take over during the next few years. In fact, such technology has also been applied to hot COG and results were even more interesting to those of cold preconditioned COG [52]. Quantitative conversions could be achieved for heavy components (e.g. toluene) at methane conversions higher than 90% [52].
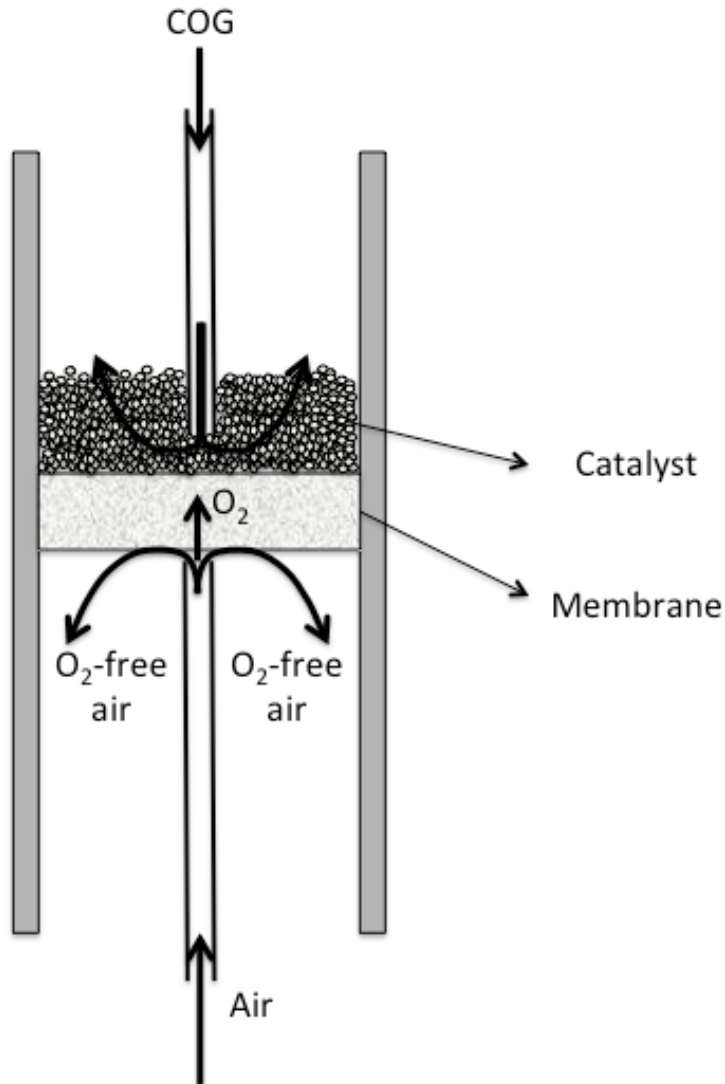
Fig. 3. Scheme of a membrane reactor for the partial oxidation of coke oven gas.

3.4. Methanol production

Most of the published works on the transformation of COG into syngas focused on the final production of hydrogen. However, an interesting alternative reported in some work deals with the use of COG-derived syngas for the synthesis of organic chemicals including methanol. The production of methanol from COG-derived syngas has been widely investigated due to its practicality in obtaining a liquid fuel instead of a gaseous product [40-42,46,85,86] as well as to the recent interest in methanol over the past years [2]. Methanol has been proposed to potentially play a key role in the future energetic model as a raw material for biofuels production of biofuels and/or hydrogen carrier in

the Hydrogen Economy. Indeed it has acquired so much importance that the Nobel Prize winner, Prof. Geroge A. Olah, has proposed Methanol Economy as an alternative to Hydrogen Economy [87, 88].

In the case of COG, the most evident example of the increased interest in methanol production from COG is the construction of several industrial plants in China to manufacture 1.2 million ton/year of methanol from COG, China being world leader in coke production (and therefore COG) [89].

COG dry reforming can be considered as the most interesting syngas production technology for methanol synthesis due to the possibility to obtain an optimum H_2/CO ratio of 2 in just one step (without the need for any preconditioning stage), as long as such dry reforming is conducted under stoichiometric conditions of CH_4 and CO_2 [40-42,47]. Moreover, the process also involves a partial recycling of the CO_2 (Figure 4) [40-42], as half of the CO_2 produced upon methanol consumption is recycled in the dry reforming process.
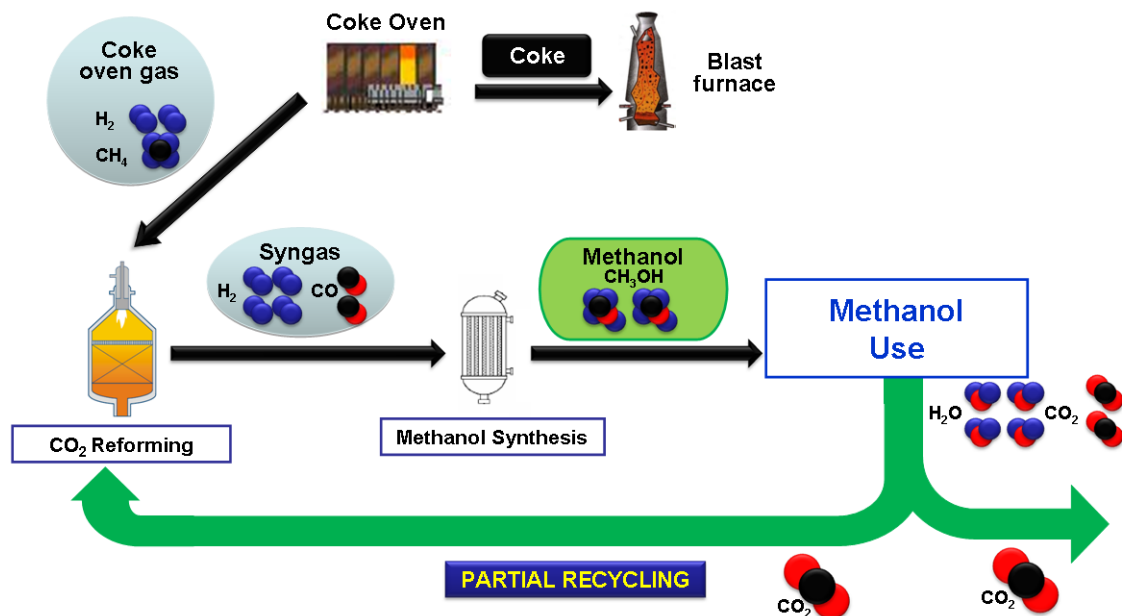

Fig. 4. Partial recycling of CO_2 in the dry reforming of coke oven gas to produce methanol for energy generation.

There are two reactions taking place in the synthesis of methanol (Reaction 11 and Reaction 12).

$2H_2 + CO \leftrightarrow CH_3OH$ (reaction 11)

$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O$ (reaction 12)

The presence of Reaction 12 imposes an additional restriction to that of H_2/CO ratio, as represented in Equation 1 [31,46,87,88,90-93]. The optimal ratio for the R parameter has been established to being the 2.03-2.05 range [88-93].

$R = (H_2 - CO_2) / (CO + CO_2)$ (Equation 1)

This R parameter gives values slightly lower than 2 when COG-derived syngas is produced by means of dry reforming [40-42]. However, as conversions in methanol synthesis are very low, the gas purge in the recycling loop that needs to be included in the process [31,90], gives rise to a hydrogen-rich gas, which can be recovered and used as fuel for the plant or to adjust the value of the R parameter [90]. A detailed thermodynamic analysis of this process was carried out by our research group [94]. Results showed that it is possible to obtain H_2/CO ratios very close to 2 and R parameter values slightly lower than 2, at high conversions and selectivities, working at temperatures higher than 800 ℃ and under stoichiometric conditions of CH_4 and CO_2 [94].

Further techno-economic studies of methanol production from COG in a Swedish plant show that this can be economically competitive with other methanol production technologies and, annual production could meet as much as 58 % of the methanol demand in the region where the plant is situated [86].

Maruoka and Akiyama [85] also studied the potential of methanol production from COG, in this case, from the exergetic point of view. They proposed an energetic integration, using the latent heat from the exhaust gases from the LD converter of the steel mill, in the reforming process of COG to produce syngas for methanol synthesis. Methanol could be produced with only 28 % of the total exergy loss experienced by the conventional methanol production process.

4. Other Technologies

The feasibility of the aforementioned technologies has been demonstrated by their already existing applications in current industrial plants [8,89]. Interestingly, there are other emerging technologies that could become important alternatives in the near future.

For example, the chemical looping combustion (CLC) of COG, with the objective to improve combustion efficiency and facilitating the capture of the CO_2 produced in the system has been proposed [95]. This technology is an elegant and energy efficient method to capture CO_2 from fuels combustion. It consists of two reactors and a circulating metal oxide that works as oxygen carrier (Figure 5). The metal oxide is reduced in the fuel reactor, then circulates to the air reactor where it is oxidised to its initial state. In this process, H_2O and CO_2 are the only combustion products and CO_2 is easier to capture as these products are not diluted with N_2 from air.
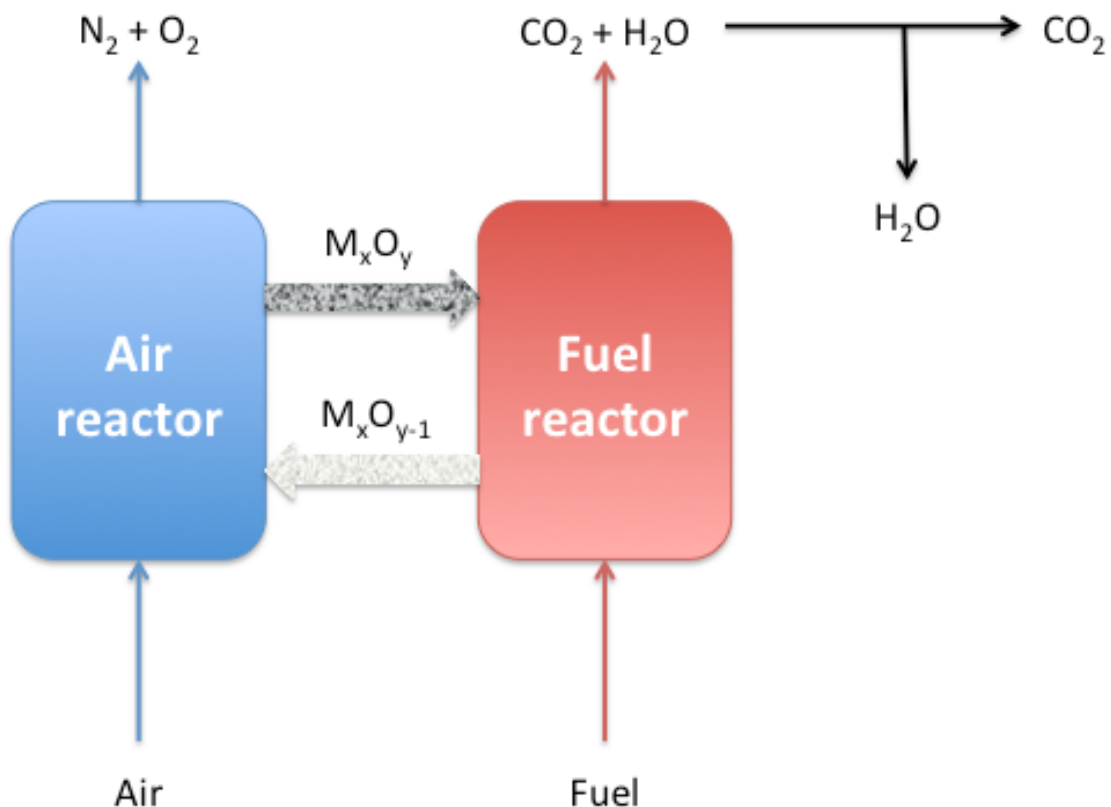

Fig. 5. Scheme of the process of chemical looping combustion.

In this work, different oxygen carriers were studied, the best results being obtained with that comprising 45% of Fe_2O_3, 15% of CuO and 40% of $MgAl_2O_4$. This carrier showed a high and stable activity over 15 reduction-oxidation cycles and achieved a maximum fuel conversion of 92% [95].

Other systems proposed during recent years are based on the combination of more than one technology. Single technologies will not be able to achieve an optimal utilisation of COG. However, combinations of such systems could possibly produce the needed synergy to improve single technologies. Several authors have recently proposed the combination of these techniques. A system in which PSA-mediated separation of hydrogen was combined with subsequent thermal upgrading of COG to produce syngas (and more H_2) was recently proposed by Wang *et al*. [96] This study also included the necessary CO_2 adsorption technology to improve hydrogen production. Such combination led to an H_2 production increase of about 9 %.

Comparatively, Jin *et al*. [97] proposed a multifunctional energy technology in which COG and coal were utilised to produce hydrogen and energy in the same system. Improved hydrogen recoveries and energy efficiencies at reduced CO_2 emissions could be obtained in the combined technology as compared to those of individual systems.

A polygeneration system in which three different chemicals (methanol, dimethyl ether and dimethyl carbonate) were produced from COG and coal gasification gas by means of an integrated catalytic synthesis procedure was also recently reported [98]. A simulation of the proposed system (with comments on improvements needed in syngas conversion and reformer design) was also included as part of this work to demonstrate the potential of the technology to efficiently produce high added value chemicals.

5. Future prospects and outlook

The steelmaking industry is the largest energy consuming manufacturing sector in the world and, therefore, it is responsible for 5-7 % of the total anthropogenic CO_2 emissions. Consequently, it is necessary for this industry to achieve the highest possible energetic efficiency and to reduce GHG emissions. A point of high interest for this purpose is coke oven gas (COG). Although this gas is used as fuel in different processes

of the steelmaking plants, there is an important surplus, which needs to be treated in order to obtain a better energetic efficiency, diminish GHG emissions and achieve higher economic benefits.

During recent years, alternative technologies for exploiting the COG surplus have attracted much attention due to the environmental, energetic and economical benefits that can be obtained from them. Table 3 summarizes the main advantages and disadvantages of all the technologies reviewed in this work. These alternatives can be divided in three main blocks: hydrogen separation, synthesis gas production and other technologies. Hydrogen separation has a huge potential since COG is a H_2-rich gas, which would allow a "green" production of H_2, since, instead of the pollution and GHG emissions characteristic of conventional H_2 production technologies, using COG as H_2 source, would eliminate the pollution resulting from its combustion. Hydrogen separation has been one of the most studied alternatives for using the COG surplus. Moreover, some of these technologies, such as PSA and membrane separation are already in use in other industrial processes, so their implantation in coking plants would not present any special difficulty. However, the H_2 recovery from COG surplus has an important drawback that needs to be overcome. With these technologies, no advantage is taken of the other gases, especially those containing carbon, i.e. CH_4, CO, CO_2 and light hydrocarbons. For this reason, H_2 separation needs to be combined with other technologies in order to exploit all of the components of the COG surplus.

For syngas production, COG is upgraded by means of the different technologies currently available (steam reforming, dry reforming and partial oxidation), making these processes interesting alternatives for H_2 amplification of the original COG or for the production of chemicals, thereby supplanting conventional production from natural gas or petroleum. Synthesis gas production from COG surplus seems to be the most interesting alternative for the use of this interesting source. The large number of processes available (steam reforming, dry reforming, partial oxidation) allows obtaining a wide variety of H_2/CO ratios (from 2 in dry reforming to nearly 5 in steam reforming), making the COG alternative highly versatile for obtaining different final chemical products. Moreover, even for the production of H_2, COG is a more interesting alternative than H_2 separation, since the hydrocarbons (CH_4 and C_nH_m) are also used. However, reforming processes are energy intense technologies, so their industrial

implantation needs to study in depth the energetic requirements and benefits. Besides, the construction of reforming plants requires a high level of capital investments.

Special attention has been paid to methanol production, due to the interest of this product as a gasoline substitute or H_2 carrier. In this case, dry reforming of COG seems to be the preferable technology, since it will require fewer process units than the other thermal upgrading technologies. In the particular case of methanol, it is already industrially implanted and. Besides, by using dry reforming as the method for the production of synthesis gas, it will be possible to partially recycle the CO_2 produced when methanol has been consumed. Moreover, the economic studies carried out on this matter, suggest that it would be economically competitive with classical methanol synthesis processes. Even so, the complete process of methanol production will require a higher level of investment and more complex facilities.

Other interesting alternatives, such as COG chemical looping combustion or the combination of two or more of the previous technologies have been proposed, though research into these systems is still in its initial stages and will need further research before considering their implantation at industrial level.

Table 3. Advantages and disadvantages of the different technologies for COG use.

Process	Technology	Advantages		Disadvantages	
Hydrogen separation	PSA	• Well developed • Easy industrial implementation	• Low energy requirement • Low operating cost • High H_2 purity	• Need of other technologies for whole exploitation of COG surplus	• Previous separation of tar, BTX, H_2S, NH_3 and light hydrocarbons
	Membranes	• Well developed • Easy industrial implementation	• Easy operation • Low capital and operating costs • Low energy requirement		• H_2 purity limited to 95 % • Less studied for H_2 separation from COG
	Hydrates	• Mild operating conditions	• No need of removing light hydrocarbons		• Low stage of development • Low H_2 concentration • Needs additives
	Cryogenic	• High purity of H_2			• Complicated process • Low stage of development
Syngas Production	Steam reforming	• Lower CO2 emissions than conventional processes • Whole exploitation of COG surplus • High versatility for the production of chemicals	• Most used and known technology • Catalysts well developed • High H_2/CO ratio • Possible use of hot COG (but quick catalyst deactivation)	• High energy requirements • High operation and capital costs	• The high H_2O/CH_4 ratios avoiding catalyst deactivation decrease energy efficiency • Mild pressures • With cold COG the complete elimination of BTX, NH_3 and H_2S is needed
	Dry reforming		• Requires lower pressure and energy • Consumption of CO_2 • $H_2/CO≈2$ (Fischer Tropsch) • Possible to avoid total H_2S elimination		• Needs complete elimination of BTX and NH_3 • No commercial catalyst
	Partial oxidation		• High energy efficiency • Higher reaction rates • Possible use of hot COG (but quick catalyst deactivation)		• Cold COG needs complete elimination of BTX, NH_3 and H_2S • High temperatures • High costs (reduced with membrane technology) • Low operation margin in the O_2/CH_4 ratio
	Methanol production		• Possible partial recycling of CO_2 • Industrially implanted • Economically competitive • Easier to handle than H_2		• Recovery of unreacted H_2 to adjust the H_2/CO ratio • Higher cost and more complex facilities
Other technologies	Chemical Looping	• Easier CO2 capture		• Low stage of developement	
	Combination	• Optimal use of COG surplus			

Acknowledgments

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