

# CO<sub>2</sub> recycling by means of reforming of coke oven gas for methanol production

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## Objectives and novelty

The steelmaking industry is the largest energy-consuming manufacturing sector. As a consequence of this, the CO<sub>2</sub> emissions from this sector account for about 5-7 % of the total anthropogenic CO<sub>2</sub> emissions. For this reason, increasing efforts are being made to find solutions that might help diminish these emissions and increase energy efficiency. A better management of the coke oven gas (COG) surplus is one of the proposed solutions<sup>1</sup>.

COG is a by-product from coking plants consisting mainly on H<sub>2</sub> (~55-60 %), CH<sub>4</sub> (~23-27 %), CO (~5-8 %), N<sub>2</sub> (~3-6 %), CO<sub>2</sub> (>2 %) along with other hydrocarbons in small proportions. Currently 20-40 % of COG produced is normally used as fuel in the actual coke ovens. However, there is an important excess which is usually burnt off in torches and even, in some cases, directly emitted to the air, giving rise to environmental problems and economical inefficiency. On this regard, several technologies have been proposed for valorising coke oven gas surplus<sup>1</sup>. Among these technologies, the alternative that is appealing more interest is syngas production<sup>1-7</sup>. The main reason of this interest is that syngas production allows maximizing the exploitation of coke oven gas surplus. Besides, the methanol production from the syngas generated from COG has attracted much attraction, because methanol is a valuable product, with an increasing market and easier to handle than syngas, since it is a liquid product at atmospheric conditions. Between the different syngas production technologies, the CO<sub>2</sub> reforming (or dry reforming) shows two important advantages for the production of methanol from COG: (i) it is possible to obtain a syngas suitable for methanol production (H<sub>2</sub>/CO≈2) in just one step, with no previous conditioning stages; and (ii) it constitutes a partial recycling of CO<sub>2</sub>, since part of the CO<sub>2</sub> emitted when methanol is used is consumed in the production process itself (Fig. 1)<sup>2-7</sup>.

However, there are almost no works dealing with CO<sub>2</sub> reforming of COG and its possible use in methanol

synthesis. In this work it is proposed, for the first time, the CO<sub>2</sub> reforming of COG surplus, with the aim of obtaining an appropriate syngas for feasible, efficient and environmental friendly methanol production.

## Results

The work has been divided in four blocks: the analysis of the thermodynamic equilibrium of the CO<sub>2</sub> reforming of COG<sup>2</sup>, the screening of different catalyst for the CO<sub>2</sub> reforming of COG<sup>3-5</sup>, the study of the microwave-assisted CO<sub>2</sub> reforming of COG<sup>6</sup> and a final comparison of the proposed process with conventional methanol production processes<sup>7</sup>.

The study of the thermodynamic equilibrium of the CO<sub>2</sub> reforming of COG<sup>2</sup> was performed with the aim of establishing the optimal conditions to maximize the yields of the process and to obtain a suitable syngas composition. It was found that these conditions are temperatures higher than 800 °C and the lowest possible pressures. In addition, the CH<sub>4</sub>/CO<sub>2</sub> ratio must be as near to the stoichiometric ratio as possible. Otherwise, the process yields are very low and/or the syngas thus obtained is not suitable for methanol production, since the H<sub>2</sub>/CO ratio (optimum value about 2) and the R parameter (Eq. 1, optimum value in the range of 2.03-2.05) values are inappropriate for this purpose. Moreover, the presence of light hydrocarbons in COG needs to be minimal to decrease deactivation rate of the catalyst.

$$R = (H_2 - CO_2) / (CO + CO_2) \quad \text{Eq. 1}$$

Once the optimal conditions were determined, different catalysts were tested for the CO<sub>2</sub> reforming of COG<sup>3-5</sup>. This was done because the CO<sub>2</sub> reforming of CH<sub>4</sub> is a heterogeneous catalytic reaction still under development, in spite of its several advantages, due to its main drawback: catalyst deactivation owing to the formation of carbon deposits. The catalyst studied were an activated carbon FY5<sup>3</sup>, an in-lab prepared Ni/Al<sub>2</sub>O<sub>3</sub> catalyst<sup>4</sup> and physical mixtures of both materials<sup>5</sup>. It was found that, besides the conventional reaction path of CO<sub>2</sub> reforming (methane decomposition

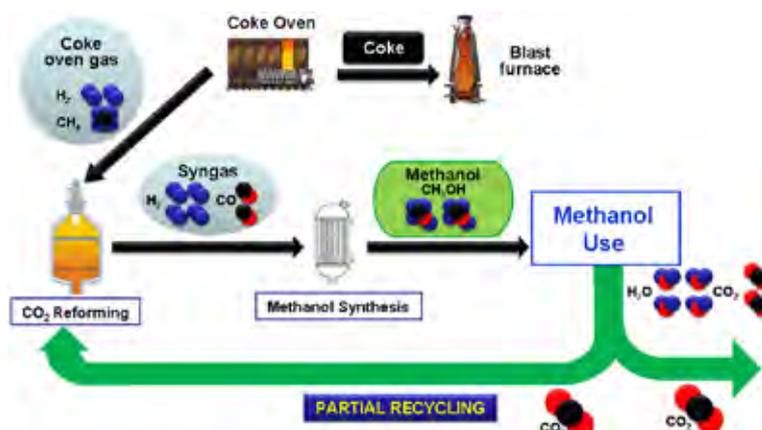
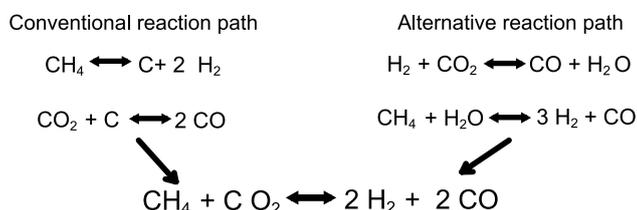


Fig. 1. Partial recycling of CO<sub>2</sub> in the production of methanol from COG through CO<sub>2</sub> reforming

followed by carbon gasification), a second reaction path takes place: the reverse water gas shift reaction followed by methane steam reforming (Scheme 1). In the case of the carbon based catalysts, it is difficult to determine the preferential path<sup>3,5</sup>, but in the case of the Ni/Al<sub>2</sub>O<sub>3</sub>, it was determined that the main reaction mechanism was the second one<sup>4</sup>. This is an important result, since the deactivation rate of the catalyst will be closer to that from the steam reforming than to that from the dry reforming, preventing deactivation. It was also found that the mixtures of AC and Ni/Al<sub>2</sub>O<sub>3</sub> presented a synergetic effect, which allowed them to achieve higher conversions and selectivities than those predicted by the Law of Mixtures<sup>4</sup>. Moreover, these mixtures also show better resistance to deactivation than the activated carbon and the Ni/Al<sub>2</sub>O<sub>3</sub> when they are used separately. Regarding to the syngas parameters (H<sub>2</sub>/CO and R parameter), activated carbon does not give rise to appropriate values<sup>3</sup> whereas the Ni/Al<sub>2</sub>O<sub>3</sub> and the mixtures give rise to values close to the optimum<sup>4,5</sup>.



**Scheme 1.** Possible reaction paths in the CO<sub>2</sub> reforming of coke oven gas.

The study of the microwave-assisted CO<sub>2</sub> reforming of COG<sup>6</sup> was performed due to the ability of microwave heating to improve catalytic heterogeneous systems, thanks to the presence of plasmas, which have a *pseudocatalytic* effect, during the dielectric heating. In the concrete case of the CO<sub>2</sub> reforming of CH<sub>4</sub>, microwave heating has been shown as a promising alternative, achieving conversions considerably higher than those obtained under conventional heating. However, when this technology is applied to the CO<sub>2</sub> reforming of COG, the conversions achieved present a contrary trend. When the activated carbon is employed as catalyst, the conversions increase in the microwave-assisted process, but in a lower extent than in the case of the CO<sub>2</sub> reforming of CH<sub>4</sub>. In the case of the mixtures of activated carbon and Ni/Al<sub>2</sub>O<sub>3</sub>, it was found that the microwave heating gives rise to lower conversions than conventional heating. To the best of our knowledge, this behaviour has been never found in heterogeneous catalytic processes. After exploring different possible causes, it was concluded that the combination of high H<sub>2</sub> proportions and microwave heating produces plasmas of very high temperatures, that promote the sintering of the catalyst, decreasing its catalytic activity.

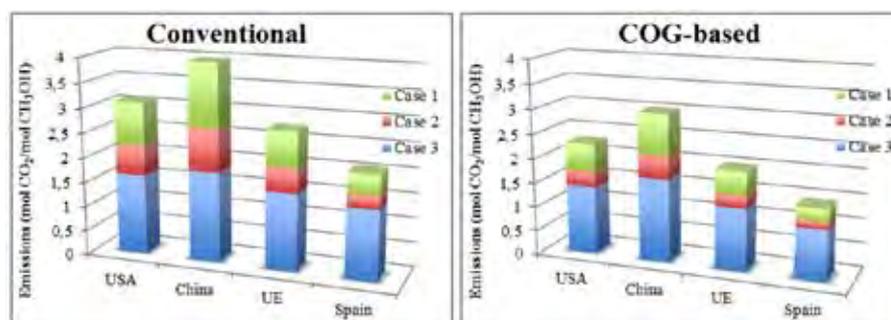
The final part of the work was an evaluation of the whole process, from the coke oven gas to the use of the methanol produced and a comparison with conventional methanol production<sup>7</sup>. The novel process shows certain advantages, the most important being lower CO<sub>2</sub> emissions. Indeed, these emissions can be reduced by as much as 30%, depending on the location of the plant and the energy integration of the process (three different cases were studied, varying the degree of energy integration). Moreover, COG-based production allows the maximum exploitation of the raw materials while purification costs are kept down to a minimum. From the energy point of view, COG-based production entails lower energy consumption than conventional production, whereas conventional production allows a higher energy recovery, which could eventually result in lower energy requirements provided that an adequate energy integration strategy is adopted.

## Conclusions

**The general conclusion of the work is that the production of methanol via the CO<sub>2</sub> reforming of COG can be a competitive process that offers several technical advantages over conventional methanol production.** Among these advantages can be highlighted the high degree of exploitation of raw materials (10% higher than conventional process) and the higher purity of the methanol produced (it does not need further purification for be used as fuel), but the main advantage of the process is the reduction in the CO<sub>2</sub> emissions in a large extent (up to 30%). In terms of energy, the COG-based process has lower energy consumption, but with conventional production higher energy recoveries are possible, which might eventually result in lower energy requirements than in the case of methanol production from COG.

## Related publications

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**Fig. 2.** CO<sub>2</sub> emissions of the conventional and the COG-based processes