New process for producing methanol from coke oven gas by means of CO_2 reforming. Comparison with conventional process

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ABSTRACT

A novel method of producing methanol from coke oven gas (COG), involving the CO_2 reforming of COG to obtain an appropriate syngas for the synthesis of methanol is proposed. This method is compared with a conventional process of methanol synthesis from natural gas, in terms of energy consumption, CO_2 emissions, raw material exploitation and methanol purity. Whereas this new process requires the consumption of less energy, the conventional process allows a higher energy recovery. CO_2 emissions are considerably lower with the new process, but the geographic situation of the plant plays a determinant role. From the point of view of raw material exploitation and methanol purity, the process proposed yields better results. These results suggest that methanol production from coke oven gas would be a more attractive alternative to conventional processes.

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1. Introduction

Methanol is one of the most important chemical materials produced today due to the wide variety of processes in which it is used [1–6]. Its applications range from chemical uses (as solvent or in the production of organic products such as formaldehyde) to energy uses (e.g., the production of biodiesel or as a fuel itself) [1,4–6]. Nowadays, methanol is manufactured using a technology based mainly on natural gas as feedstock, although some processes use oil [4,7].

This process involves four steps: syngas generation, compression, the synthesis of methanol and distillation [4]. Syngas generation and methanol synthesis are the areas of increasing scientific development. In a conventional methanol plant, syngas generation accounts for 55% of the financial outlay required for the process units [4]. Different syngas production processes are available depending on the characteristics of the natural gas and the economic restraints imposed on the plant [2,4,7–13]. These processes are steam reforming, autothermal reforming, and combined reforming. However, in the last few years an alternative source of syngas production has emerged: coke oven gas [14–23]. COG is a by-product from coking plants, consisting mainly of H_2 (55–60%), CH_4 (23–27%), CO (5–8%) and N_2 (3–5%) along with other hydrocarbons, H_2S and NH_3 in small proportions. Most of this gas is used as fuel in the coke ovens, but usually there is a surplus of gas which is used in other processes of the plant, or is simply burnt away in torches [16,23–27], giving rise to environmental problems, in the form of greenhouse gas emissions. The thermal upgrading of COG would provide an ideal

solution to these environmental problems. However, none of the previously mentioned processes for syngas production from natural gas can be used if the final product is methanol. This is due to the high H_2/CO ratios and R parameters (Eq. 1) resulting from these processes if the coke oven gas is used as the source of methanol production [15,18,20,21,23].

$$R, \text{dimensionless} = (H_2 - CO_2)/(CO + CO_2) \qquad (1)$$

In order for the syngas to be used for the production of methanol the H_2/CO ratio needs to be around 2 whereas the optimum value for the R parameter lies within the range of 2.03–2.05 [1,2,28]. A possible solution to this problem could be to generate the syngas by means of CO_2 reforming (or dry reforming). CO_2 reforming is a reaction between CO_2 and CH_4 that gives rise to H_2 and CO (Reaction 1).

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \qquad (Reaction 1)$$

By applying CO_2 reforming to the coke oven gas, under stoichiometric conditions of methane and carbon dioxide, it is possible to obtain a syngas with a H_2/CO ratio and an R parameter slightly lower than the optimum values. Only minor adjustments of these values would then be required, and this can be done using the H_2 recovered at the end of the process of methanol production [18]. Moreover, the production of methanol from coke oven gas via CO_2 reforming could be considered as a "partial recycling" of carbon dioxide, since half of the carbon dioxide produced, when methanol is used, is consumed during the production process itself [15,18,20,21,23]. This balance is illustrated in Fig. 1.

However, this advantage has yet to be demonstrated, as it is possible that the yields and the energy needs of the process will affect the abovementioned balance. Moreover, no references can be found in the
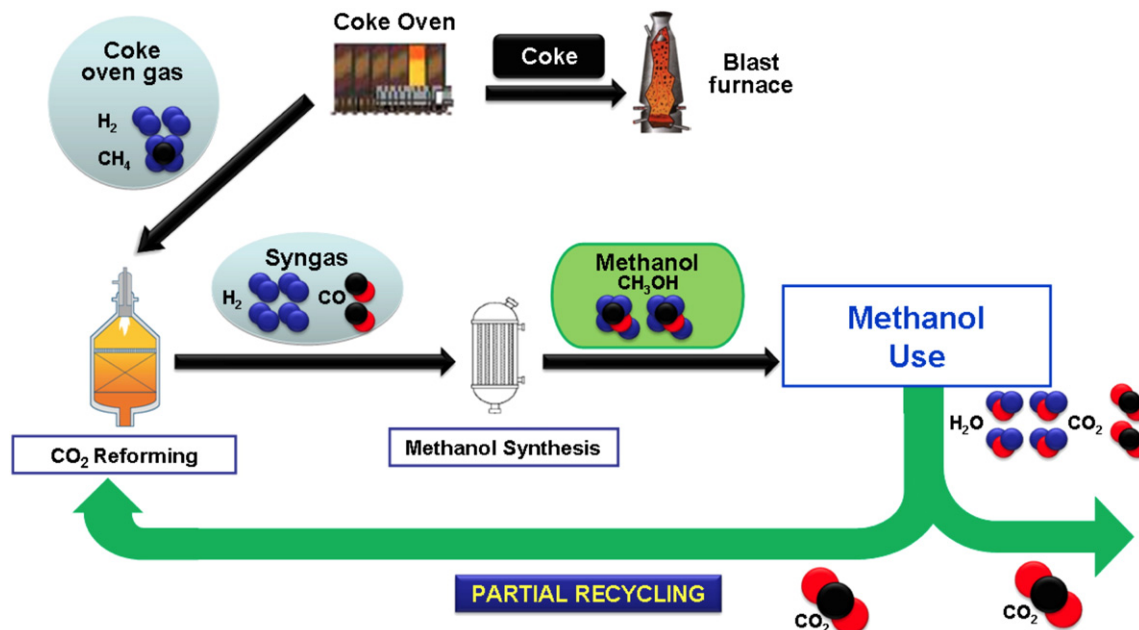

Fig. 1. Partial recycling of CO_2 in the synthesis of methanol from COG via dry reforming.

literature to any previous comparison of this technology with that of conventional methanol production. Hence, the aim of the present work is to carry out a comparative simulation analysis of methanol production from coke oven gas via dry reforming and the conventional process of methanol production from natural gas, using Aspen Plus® software.

2. Simulation methodology

Two different processes were studied: the conventional production process (CP) and the novel technology proposed for the dry reforming of coke oven gas (DR-COG). These processes were modelled using Aspen Plus® software. In each process a flow rate basis of 1 kmol/h of feed gas, natural gas or coke oven gas, was employed. The compositions of these gases are shown in Table 1.

2.1. CP process model

In the CP process, which is the most widespread methanol production process in use, the natural gas is fed into a reformer where the methane reacts with excess steam through a steam reforming reaction. Since the H_2/CO ratio and the R parameter of the syngas obtained are higher than that desired, the syngas is fed into a second reactor where it reacts with O_2 through partial oxidation. In this way, the H_2/CO ratio and the R parameter are adjusted to the desired values. Since there is a surplus of H_2O that has not reacted in the first reactor, a condensation stage is required to separate the excess water. The syngas is then introduced into the methanol synthesis loop. Recirculation is

Table 1
Natural gas and coke oven gas compositions used in the simulation.

Component	Natural gas (vol.%)	Coke oven gas (vol.%)
CH_4	91.2	26.0
H_2	0	62.0
CO_2	1.0	1.5
CO	0	7.0
N_2	0.5	2.2
C_2H_6	6.4	0.5
C_3H_8	0.8	0
C_4H_{10}	0.1	0
C_2H_4	0	0.8

required because the conversion in each cycle is very low. A purge is included in the loop to prevent the accumulation of inerts.

The model developed for this study (Fig. 2) is composed of:

1. A line of compressed natural gas (NG), the composition of which is shown in Table 1.
2. A line of steam production (WATER).
3. A steam reformer (REFORMER) where the NG and WATER react to give rise to the initial syngas (SYNGAS1), the composition of which is still far from that required for methanol production.
4. A line of compressed O_2 (O2-LP).
5. A partial oxidation reactor (POX) where the SYNGAS1 and O2-LP react to give rise to a second syngas. After the excess of water has been separated this syngas is compressed (SYNGAS2) and introduced into the recycling loop.
6. Inside the recycling loop there is a methanol synthesis reactor (SYNTHES) and next a condenser where the products are separated from the unreacted gases (CONDENS2). The unreacted gas stream is split by means of a purge (PURGE) into two streams, the purge stream (PURGE) and a stream of recycled products (RECYCLE1) which are compressed (RECYCLE1) before being mixed with SYNGAS2.

Table 2 shows the operation conditions, which have been selected on the basis of available bibliographic data, corresponding to the main units of the process, i.e. steam reforming [2,4,7], partial reforming reactor [2,4,29,30] and methanol synthesis reactor [1,2,4,7,29,31].

2.2. DR-COG process model

Fig. 3 shows a block diagram of the DR-COG process. In this case there is only one reactor, since it is possible to obtain a suitable syngas in one step. There is then a double loop: one for the recirculation and the other for recovering unreacted H_2 so that the values of the R parameter and the H_2/CO ratio can be adjusted.

Fig. 4 shows the model developed using Aspen Plus®.

This model is composed of:

1. Two initial streams of CO_2 (CO2) and coke oven gas (COG), the composition of which is shown in Table 1.
2. A dry reformer where CO_2 and COG react to give rise to the synthesis gas (SYNGAS1), the composition of which is adjusted using the