

Syngas Production through Dry Reforming of Raw Bio-oil: Effect of CO₂/C Ratio

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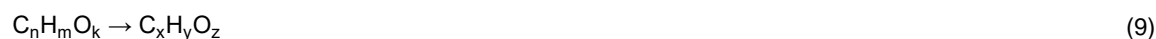
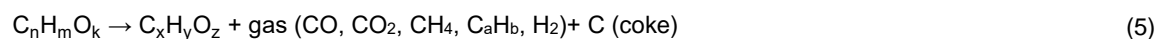
This study deals with the effect of CO₂/carbon molar ratio (CO₂/C) on syngas production in the dry reforming (DR) of real bio-oil with a NiAl₂O₄ spinel derived catalyst, which has high activity and H₂ selectivity in the raw bio-oil reforming. The reaction tests were carried out at 700 °C, steam/carbon (S/C) molar ratio of 0.4 (corresponding to the water contained in the bio-oil feed), space time of 0.25 g_{catalyst}h/g_{oxygenates}, and CO₂/C ratio of 0, 0.5 and 1. The results evidence a higher syngas yield in the DR reaction tests (88%, not dependent on CO₂/C ratio) compared to the conventional steam reforming (SR, 76%) because of the increase in CO yield, which leads to a decrease in H₂/CO ratio (from 1.8 in SR to 1.2 and 1 for CO₂/C ratio of 0.5 and 1, respectively). For both CO₂/C ratios positive CO₂ conversions (22-24 %) and a reduction of CO₂ emissions over SR are obtained. The characterization of spent catalysts by several techniques proves that the main cause of deactivation is coke deposition, that is mainly composed of structured carbon (filamentous carbon), with a small fraction of amorphous coke. The DR reaction tests lead to a noticeable higher deposition of filamentous carbon, which does not lead to a noticeable difference in the catalyst stability compared to SR, in spite of the significant higher amount of coke deposited (34 and 46 wt% for CO₂/C ratios of 0.5 and 1, respectively) than in the SR (18 wt%).

1. Introduction

The increasingly strict environmental policies aimed at mitigating the climate damage caused by CO₂ emissions resulting from the consumption of finite fossil fuels has attracted increasing attention on the development of alternative and clean technologies that use renewable energy sources as raw material (Sharma et al., 2022). In this scenario, the use of hydrogen, as a clean energy vector, emerges (Espregren et al. 2021) and its production from sustainable and CO₂ neutral biomass is of major interest as an alternative strategy to H₂O electrolysis (Kim et al. 2021), as it can be integrated into energy and economic policies to improve the management of forestry and agricultural waste with a neutral CO₂ balance (Lepage et al. 2021). Steam Reforming (SR) of raw bio-oil (obtained from fast pyrolysis of biomass) is a promising and economically viable technology that is attracting increasing interest (Lopez et al. 2022) as it enables the joint valorization of the complex mixture of oxygenated organic compounds contained in bio-oil avoiding the costly separation of the high water content (Valle et al. 2019). SR is the reforming process that allows producing the highest H₂ yield from bio-oil, but it also produces a high CO₂ yield. Alternatively, the conversion of bio-oil into syngas (mixture of H₂+CO) useful for the production of chemicals and fuels has motivated the interest in the dry reforming (DR, with CO₂) of bio-oil, which, in addition, reduces CO₂ emissions by forming CO (through reverse water-gas-shift (WGS) reaction) (Saravanan et al. 2021). This process has as a close reference the development of DR or combined steam/dry reforming (CSDR) of CH₄/biogas for the production of syngas, intensively studied in the literature (Guilhaume et al. 2021; Buasuk et al. 2021; Dan et al. 2021). Hu and Lu (2010) pioneered the proposal to couple the most common bio-oil reforming technologies (SR, partial oxidation (POX) and oxidative steam reforming (OSR)) with CO₂ reforming (DR) in order to produce a useful syngas for chemical synthesis and, in addition, as an environmentally friendly and efficient method for CO₂ valorization. Recently, other authors have tackled the DR or CSDR of bio-oil, either with thermodynamic studies (Xie et al. 2020) or experimental works with model compounds of bio-oil or their

mixtures (simulated bio-oil) (Fu et al., 2016; Yao et al., 2019; Xu et al., 2020;) and more scarcely with real bio-oil (Yao et al., 2018; Xu et al., 2019).

The overall reaction for the SR of bio-oil (Eq. (1)) is a combination of the reforming reaction to produce (CO+H₂) (Eq. (2)) and the subsequent WGS reaction (Eq. (3)). The DR reaction of bio-oil is given by Eq. (4). Nonetheless, other parallel secondary reactions take place, such as decomposition/cracking of oxygenates (Eq. (5)), reforming (steam and dry) of decomposition products (CH₄ and light hydrocarbons (C_aH_b), Eqs. (6), (7) and (8), respectively) and interconversion of oxygenates (Eq. (9)). Moreover, the catalyst undergoes rapid deactivation mainly due to coke deposition, whose amount depends on the relative importance of the reactions for its formation and gasification (Eqs. (10)-(12)).



The objective of this work is to study the effect of CO₂/C ratio (0 (conventional SR), 0.5 and 1) upon the syngas production and composition, and catalyst stability in the DR of raw bio-oil with a NiAl₂O₄ spinel derived catalyst, which has high activity and H₂ selectivity in the raw bio-oil SR and can be fully regenerated by combustion at 850 °C (Remiro et al. 2018). For that purpose, the evolution with reaction time of syngas yield, H₂/CO molar ratio, CO₂ conversion and reduction of CO₂ emissions were analyzed. Besides, the nature and amount of coke deposited, and structural and physical properties of the spent catalyst were characterized by Temperature Programmed Reduction (TPR), X-Ray Diffraction (XRD), N₂ adsorption-desorption, Temperature Programmed Oxidation (TPO) and Scanning Electron Microscopy (SEM) images, in order to explain the deactivation behavior in the combined process.

2. Experimental

2.1 Raw bio-oil

The raw bio-oil (synthesized by fast pyrolysis of pine sawdust) was supplied by BTG Bioliquids BV (The Netherlands). Its main properties are the following: water content, determined by using Karl-Fischer titration (KF-Titrino Plus 870), 24 wt%; density, 1.201 g/ml; viscosity at 40 °C, 250 cP (Brookfield DV2T Ametek); pH, 2.5-3.5 and empirical formula C_{4.6}H_{6.2}O_{2.4} (water-free basis), obtained by CHO analysis (Leco CHN-932 analyzer). The chemical composition was determined by gas chromatography/mass spectrometer (GC/MS) analysis on a Shimadzu GC/MS-QP2010S, provided with a BPX-5 column (50 m x 0.22 mm x 0.25 μm), and a mass selective detector. The main components are acetic acid (16.6 wt%), levoglucosane (11.1 wt%), guaiacol (11.1 wt%) and acetol (9.4 wt%).

2.2 Catalyst

The catalyst precursor (Ni-Al spinel, with a nominal Ni content of 33 wt%) was synthesized by co-precipitation method (Arandia et al. 2020), mixing aqueous solutions of hexa-hydrated nickel nitrate and aluminum nitrate nonahydrate with a 0.6 M solution of ammonium hydroxide as a precipitating agent at 25 °C and pH of 8. After

aging for 30 min, the precipitate was filtered, washed with distilled water, dried at 110 °C for 24 h, calcined at 850 °C for 4 h and finally, crushed and sieved to obtain particle sizes in the range of 150-250 µm.

The physical properties (Brunauer–Emmett–Teller (BET) surface area, pore volume and mean pore diameter) of the fresh (reduced) and spent catalysts were characterized by adsorption-desorption of N₂ (Micromeritics ASAP 2010). TPR analysis (Micromeritics AutoChem II 2920) was carried out for determining the reducibility of the metal species. XRD analysis (Bruker D8 Advance diffractometer with a CuKα1 radiation) was used to calculate the average Ni crystal size of fresh (reduced) and used catalysts (using Scherrer equation at 2θ=51.8 °) and the crystalline state of coke deposits. The amount and nature of coke deposited on used catalyst samples was determined by TPO (TA-Instruments TGA-Q5000IR thermobalance), coupled in line with a mass spectrometer (Thermostar Balzers Instrument) for monitoring the CO₂ signal because the oxidation of Ni during combustion masks the thermogravimetric signal. SEM images of the fresh or used catalysts were obtained in a Hitachi S-4800 N field emission gun scanning electron microscope with an accelerating voltage of 5 kV and secondary electron detector (SE-SEM) and a Hitachi S-3400N microscope with an accelerating voltage of 15 kV using a backscatter electron detector (BSE-SEM).

2.3 Reaction equipment, operating conditions and reaction indices

The kinetics reaction tests were carried out in an automated reaction equipment (MicroActivity-Reference, PID Eng & Tech) with two units in series, for bio-oil volatilization (thermal treatment) (Unit 1) and for SR (no CO₂ addition) or DR reactions (Unit 2). In Unit 1 (a U-shaped steel tube with inner diameter of 19 mm, heated at 500 °C), a controlled deposition of a solid residue (pyrolytic lignin) occurs during bio-oil volatilization, formed by repolymerization of some oxygenated compounds in the raw bio-oil (mainly phenolic compounds). The volatile oxygenates leaving Unit 1 constitute the treated bio-oil, that enters the Unit 2, which consists of a stainless steel fluidized-bed reactor (22 mm of internal diameter, total length of 460 mm and effective hot length of 100 mm). The catalytic bed is located over a layer of quartz wool and consists of the catalyst mixed with inert solid (SiC, with particle size of 75 µm), in order to improve the fluid dynamic regime in the bed. An injection pump (Harvard Apparatus 22) was used for feeding the bio-oil (0.06 ml/min). The reaction products were analyzed in a Micro GC Varian CP-490 connected in-line to the reactor through an insulated line (130 °C) to avoid condensation of the products, and equipped with three analytic channels: molecular sieve MS5 for quantifying H₂, O₂, N₂, CH₄ and CO; PPQ column for light hydrocarbons (C₂-C₄), CO₂ and water; and Stabilwax for oxygenated compounds (C₂⁺) and water. Prior to each reaction, the NiAl₂O₄ spinel is reduced in situ under a H₂-N₂ (10 vol% H₂) at 850 °C for 4 h, thus obtaining the active Ni metallic phase well-dispersed on the alumina support. The experiments were carried out at atmospheric pressure and 700 °C, with S/C of 0.4 (corresponding to the water contained in the bio-oil feed), CO₂/C of 0 (conventional SR), 0.5 and 1, and space time of 0.25 g_{catalyst}/h/g_{oxygenates}. The results were quantified with the following indices: the syngas yield (Eq. (13)), H₂/CO molar ratio (Eq. (14)), CO₂ conversion (Eq. (15)) and reduction of CO₂ emissions (Eq. (16)):

$$Y_{H_2+CO} = \frac{F_{H_2} + F_{CO}}{F_{H_2+CO}^0} \cdot 100 \quad (13)$$

$$H_2/CO = \frac{F_{H_2}}{F_{CO}} \quad (14)$$

$$X_{CO_2} = \frac{F_{in, CO_2} - F_{out, CO_2}}{F_{in, CO_2}} \cdot 100 \quad (15)$$

$$R_{CO_2} = \frac{(F_{out, CO_2 (SR)} + F_{in, CO_2}) - F_{out, CO_2 (DR)}}{(F_{out, CO_2 (SR)} + F_{in, CO_2})} \cdot 100 \quad (16)$$

Where, F_{H₂} and F_{CO} is the H₂ and CO molar flowrate in the product stream; F_{H₂+CO}⁰ is the H₂+CO stoichiometric molar flowrate, calculated as (n+(n+m/2-k))/n·F_{in} (Eq. (2)), with F_{in} being the C molar flowrate of oxygenates at the reactor inlet (Unit 2); F_{in, CO₂} is the molar flowrate of CO₂ in the initial input and F_{out, CO₂} the molar flowrate of CO₂ in the reformed products; F_{out, CO₂ (SR)} and F_{out, CO₂ (DR)} are the molar flowrate of CO₂ at the outlet of the SR and DR process, respectively. In the definition of the reduction of CO₂ emissions, the CO₂ flow at the reactor inlet in the DR process (F_{in, CO₂}) was considered, since if not used in this process it would contribute to the total CO₂ emissions in the factory.

3. Results

Figure 1 shows the evolution with time on stream (TOS) of syngas yield, H₂/CO ratio, CO₂ conversion and reduction of CO₂ emissions in the DR process compared to the SR unit. The results show a slow and progressive

drop of syngas yield (Figure 1a) over reaction time evidencing a progressive catalyst deactivation, being slightly slower without CO₂ addition. A small CO₂ addition (CO₂/C=0.5) leads to a higher syngas yield (88%) compared to the conventional SR (76%), that can be attributed to the increase in CO and H₂ yields caused by the CH₄ dry reforming (Eq. (7)), with a decrease in the H₂/CO ratio (1.2) in comparison to SR (1.8) due to the promotion of reverse WGS (Eq. (3)) reaction. However, a further addition of CO₂ (CO₂/C=1) does not improve syngas yield, although H₂/CO ratio still decreases slightly, to 1, which is useful for dimethyl ether (DME), acetic acid or ethanol syntheses and oxo-synthesis (Salaudeen et al, 2018). Moreover, a positive CO₂ conversion is attained for both CO₂/C ratios (between 22-24% at zero time), which means that the CO₂ is effectively being converted in the DR process, and interestingly, with a greater stability for the highest CO₂/C ratio. The lower CO₂/C ratio leads to a higher initial value of reduction of CO₂ emissions compared to SR process (38%), but it decreases steadily due to the faster deactivation, whereas almost constant 32% reduction of CO₂ emissions is obtained with CO₂/C=1.

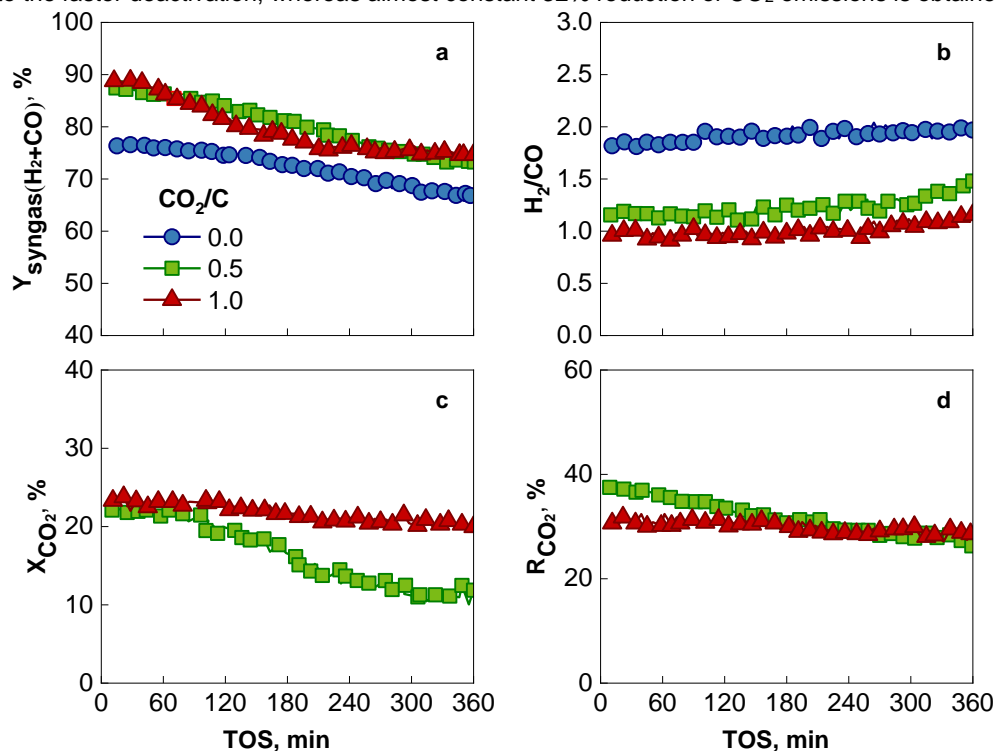


Figure 1: Effect of CO₂/C ratio on the evolution with TOS of syngas (H₂+CO) yield (a), H₂/CO ratio (b), CO₂ conversion (c) and reduction of CO₂ emissions (d) in the SR (blue circles) and DR (green squares and red triangles) of raw bio-oil. Conditions: 700 °C, S/C=0.4, space time=0.25 g_{catalyst}/g_{oxygenates}.

In order to explain the differences in stability indicative of catalyst deactivation, the spent catalyst samples were characterized by several techniques to determine possible changes in Ni oxidation state and crystal size, in the porous structure, and the amount and characteristics of coke deposits. Ni oxidation was ruled out as deactivation cause, as no significant reduction peaks were observed in the H₂-TPR profiles of used catalysts (not shown), nor NiO species in their XRD diffractograms (Figure 2a). The absence of oxidized species is due to the highly reducing environment in the reforming reaction tests, with a high H₂ content. The sintering of Ni crystals was also ruled out as deactivation cause as there is a very small increase in the average Ni⁰ particle size (Table 1) of the used catalysts (in the 16.0–21.0 nm range) compared to the fresh (reduced) catalyst (15.0 nm) and, moreover, the increase in crystal size does not either correlate with the stability observed. Consequently, coke deposition is the main deactivation cause. The TPO profiles of all the used catalysts (Figure 2b) show a main combustion peak around 590 °C (SR) and 600 °C (DR reaction tests) and a small peak burning below 500 °C, the former being attributable to structured carbon (filamentous carbon), whereas the latter is amorphous coke (Arandia et al., 2020; Valle et al., 2019). The presence of carbon filaments is coherent with the increase in BET surface area for the used catalysts samples compared to the fresh (reduced) catalyst (Table 1), that evidences the presence of a porous coke structure, and also by SEM images of the used catalysts (Figure 3). The addition of CO₂ significantly increases the coke deposition (34 and 46 wt%, for CO₂/C ratios of 0.5 and 1, respectively), compared to the SR (18 wt%), being the filamentous coke the most promoted. The higher increase in the BET surface area (Table 1), the observation of more crystalline coke structures in the XRD diffractograms (diffraction

peak at $2\theta = 26^\circ$ in Figure 2a) and the higher amount and more homogenous carbon filaments observed in the right image of Figure 3 (DR reaction test) compared to the thinner, loose and short carbon filaments observed in the left image (SR reaction test), give evidence of a higher formation of filamentous coke with the increase in CO_2/C ratio. This should be most probably attributable to the promotion of Boudouard reaction due to the higher CO concentration in the reaction medium.

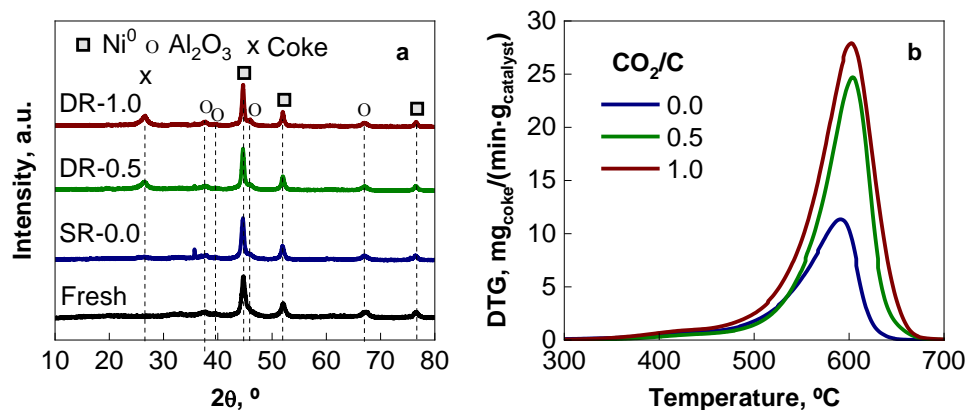


Figure 2: XRD diffractograms for fresh and used catalysts (a) and TPO profile for used catalysts (b).

Table 1: Physico-chemical properties of the fresh and spent catalysts in SR and DR processes.

Catalyst	Processes	CO_2/C	d_{Ni} (nm)	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	d_{pore} (nm)
Fresh (reduced)	-	-	15	65.1	0.24	13.1
	SR	0	16	77.5	0.18	9.7
Spent	DR	0.5	17	94.0	0.18	9.1
		1.0	21	123.0	0.29	12.3

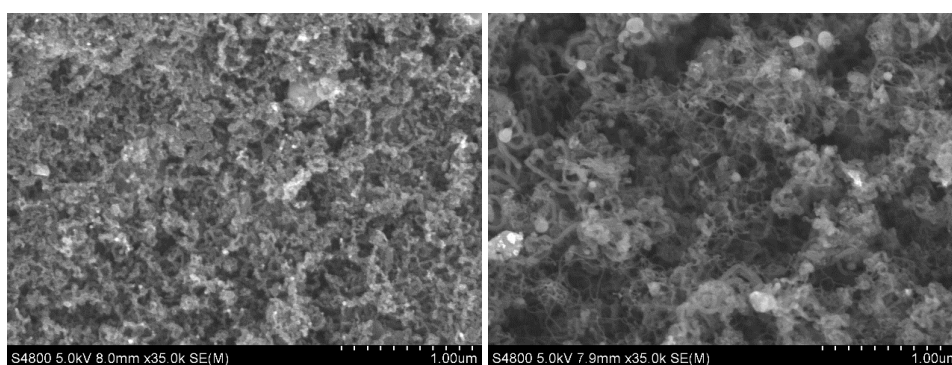


Figure 3: SEM images of the catalyst used in SR (left) and DR (CO_2/C ratio of 1) (right) processes.

4. Conclusions

The DR of bio-oil at 700°C with low CO_2 addition allows to obtain a high yield of syngas with slightly tuneable H_2/CO ratio depending on the CO_2/C ratio, with values of 1.2-1 (for CO_2/C of 0.5-1, respectively), the latter useful for production of DME, acetic acid or ethanol and oxo-synthesis. In spite of the higher amount of coke deposited compare to conventional SR process, it is mainly of filamentous nature, which does not lead to a significant more rapid deactivation than in the SR. Moreover, CO_2 conversions between 22-24% are obtained, with reduction of CO_2 emissions in the 32-38% range compared to SR. Consequently, DR of bio-oil can be envisioned as a green process for syngas production and effective method for CO_2 valorization.

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