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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 ºC, steam/carbon (S/C) molar ratio of 0.4 (corresponding to the water contained in the bio-oil feed), space time of 0.25 gcatalysth/goxygenates, 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 (Espegren 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 (CaHb), 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)).

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| $$C\_{n}H\_{m}O\_{k} + (2n-k)H\_{2}O\rightarrow nCO\_{2}+ (2n+\frac{m}{2}-k)H\_{2}$$ | (1) |
| $$C\_{n}H\_{m}O\_{k} + (n-k)H\_{2}O \rightarrow nCO + (n+\frac{m}{2}-k)H\_{2}$$ | (2) |
| $$CO + H\_{2}O \leftrightarrow CO\_{2} + H\_{2}$$ | (3) |
| $$C\_{n}H\_{m}O\_{k} + xCO\_{2}\rightarrow (n+x)CO + (\frac{m}{2}-x)H\_{2}+\left(x+k\right)H\_{2}O$$ | (4) |
| $C\_{n}H\_{m}O\_{k} \rightarrow C\_{x}H\_{y}O\_{z} + gas (CO, CO2, CH4, CaHb, H2)+ C$ (coke)  | (5) |
| $$CH\_{4}+ H\_{2}O \leftrightarrow CO + 3H\_{2}$$ | (6) |
| $$CH\_{4}+ CO\_{2} \leftrightarrow 2CO + 2H\_{2}$$ | (7) |
| $$C\_{a}H\_{b} + aH\_{2}O \rightarrow aCO + \left(a +b/2\right)H\_{2}$$ | (8) |
| $$C\_{n}H\_{m}O\_{k} \rightarrow C\_{x}H\_{y}O\_{z}$$ | (9) |
| CH4 → 2H2 + C | (10) |
| 2CO ↔ C + CO2 | (11) |
| C + H2O → CO + H2 | (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 ºC (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.

* 1. Experimental
		1. Raw bio-oil

The raw bio-oil (synthetized 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 ºC, 250 cP (Brookfield DV2T Ametek); pH, 2.5-3.5 and empirical formula C4.6H6.2O2.4 (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 m 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%).

* + 1. Catalyst

The catalyst precursor (Ni-Al spinel, with a nominal Ni content of 33 wt%) was synthetized 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 ºC and pH of 8. After aging for 30 min, the precipitate was filtered, washed with distilled water, dried at 110 ºC for 24 h, calcined at 850 ºC 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 2=51.8 º) 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).

* + 1. 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 ºC), 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 ºC) 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 ºC 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 ºC, 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 gcatalysth/goxygenates. 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)):

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| $$Y\_{H\_{2}+CO}=\frac{F\_{H\_{2}}+F\_{CO}}{F\_{H\_{2}+CO}^{o}}·100$$ | (13) |
| $$H\_{2}/CO=\frac{F\_{H\_{2}}}{F\_{CO}}$$ | (14) |
| $$X\_{CO\_{2}}=\frac{F\_{in, CO\_{2}}-F\_{out, CO\_{2}}}{F\_{in, CO\_{2}}}·100$$ | (15) |
| $$R\_{CO\_{2}}=\frac{(F\_{out, CO\_{2} (SR)}+F\_{in, CO\_{2}})-F\_{out, CO\_{2} (DR)}}{(F\_{out, CO\_{2} (SR)}+F\_{in, CO\_{2}})}·100$$ | (16) |

Where, FH2 and FCO is the H2 and CO molar flowrate in the product stream; $F\_{H\_{2}+CO}^{o}$, is the H2+CO stoichiometric molar flowrate, calculated as (n+(n+m/2-k))/n·Fin (Eq. (2)), with Fin being the C molar flowrate of oxygenates at the reactor inlet (Unit 2); Fin, CO2 is the molar flowrate of CO2 in the initial input and Fout, CO2 the molar flowrate of CO2 in the reformed products; Fout, CO2 (SR) and Fout, 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 (Fin, CO2) was considered, since if not used in this process it would contribute to the total CO2 emissions in the factory.

* 1. 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 improves 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 ºC, S/C=0.4, space time=0.25 gcatalysth/goxygenates.*

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 ºC (SR) and 600 ºC (DR reaction tests) and a small peak burning below 500 ºC, 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 2θ = 26 º 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 CO2/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.

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| --- | --- | --- | --- | --- | --- | --- |
| Catalyst  | Processes | CO2/C | dNi (nm) | SBET (m2/g) | Vpore (cm3/g) | dpore (nm) |
| Fresh (reduced) | - | - | 15 | 65.1 | 0.24 | 13.1 |
| Spent | SR | 0 | 16 | 77.5 | 0.18 | 9.7 |
| DR | 0.51.0 | 1721 | 94.0123.0 | 0.180.29 | 9.112.3 |

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Figure 3*: SEM images of the catalyst used in SR (left) and DR (CO2/C ratio of 1) (right) processes.*

* 1. Conclusions

The DR of bio-oil at 700 ºC with low CO2 addition allows to obtain a high yield of syngas with slightly tuneable H2/CO ratio depending on the CO2/C ratio, with values of 1.2-1 (for CO2/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, CO2 conversions between 22-24% are obtained, with reduction of CO2 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 CO2 valorization.

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