

Effect of operating conditions in oxidative steam reforming of raw bio-oil with Ni spinel catalyst

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Highlights

- Catalyst deactivation is attenuated by increasing temperature (up to 700 °C) and O/C ratio
- H₂ yield at zero time is hardly affected by temperature but decreases with O/C ratio
- Coke deposition rate decreases with temperature (which affects coke nature) and O/C ratio
- Ni sintering is a significant deactivation cause at 750 °C

1. Introduction

The technological development of sustainable H₂ production routes from sources alternative to oil has a great interest in order to meet the increasing energy demand, thus avoiding the negative environmental impact of current technologies [1]. Furthermore, the implementation of reforming routes for biomass derived oxygenates, such as bio-oil (obtained by fast pyrolysis of lignocellulosic biomass), may be efficient for reducing greenhouse gas emissions [2]. The bio-oil steam reforming proceeds according to the following global stoichiometry: $C_nH_mO_k + (2n-k)H_2O \rightarrow nCO_2 + (2n+m/2-k)H_2$. The operation under oxidative steam reforming (OSR) conditions (with both O₂ and water in the feed) has the advantage of diminishing the energetic requirements of endothermic reforming reaction and attenuating coke formation [3], but involves a decrease in H₂ yield. The aim of this work is to delimit the suitable reaction conditions (temperature and oxygen/carbon (O/C) ratio) for maximizing high H₂ yield with high stability and in the OSR of raw bio-oil with a Ni spinel type catalyst (NiAl₂O₄), which was selected due to its high thermal stability.

2. Methods

The bio-oil was obtained by fast pyrolysis of pine sawdust and provided by Biomass Technology Group (BTG, Holland). The catalyst (with 33 wt% Ni, denoted CP33) was obtained from a NiAl₂O₄ precursor prepared by the co-precipitation method [4], which was calcined at 850 °C for 4 h and sieved between 125-250 μm. The kinetic runs have been performed in automated reaction equipment (Microactivity Reference) provided with two units in series (thermal step and catalytic step). The thermal step was conducted at 500 °C for vaporization of bio-oil and controlled deposition of a solid residue (15 wt % of the raw bio-oil) formed by repolymerization of the oxygenates derived from lignin pyrolysis. In the second unit (fluidized bed reactor) the catalyst is mixed with an inert solid (SiC) in order to ensure a correct fluidization regime. Prior to each kinetic run, the catalytic bed is reduced at 850 °C for 4 h. The kinetic runs have been carried out at 600-750 °C range, oxygen/carbon (O/C) molar ratio of 0.15-0.5 range, steam/carbon (S/C) molar ratio of 6 and space time of 0.15 g_{catalyst} h/g_{bio-oil}. The product stream is analyzed in-line with a microGC Varian CP 490 equipped with 4 analytic channels. The fresh and deactivated catalysts have been characterized by: adsorption-desorption of N₂ in an Autosorb iQ2 equipment from Quantachrome for calculating the BET specific surface area, pore volume and mean pore diameter; Temperature Programmed Reduction (TPR) in a Micromeritics AutoChem 2920 for determining the reducibility of the metal species; X ray diffraction (XRD) in a Bruker D8 Advance diffractometer for determining the different crystal phases present in the material. The amount and nature of coke deposited on the used catalysts has been determined by Temperature Programmed Oxidation (TPO) in a TA Instrument Q5000 thermobalance.

3. Results and discussion

The temperature effect on the evolution of reaction indices (bio-oil conversion, $X_{\text{Bio-oil}}$, and H_2 yield) is shown in Figure 1a. At zero time, the reaction indices are hardly affected by temperature due to the control of thermodynamic regime. However, H_2 yield slightly decreases above 700 °C, whereas CO yield increases (not shown) due to the promotion reverse water-gas-shift (r-WGS) reaction at high temperatures. Furthermore, a rapid drop in conversion and H_2 yield is observed at 600 °C, which is evidence of a fast catalyst deactivation, rapidly approaching the values obtained by thermal routes (without catalyst). The increase in temperature up to 700 °C attenuates catalyst deactivation, whereas a further increase up to 750 °C does not involve a further improvement in catalyst stability. The results on the effect of O/C ratio on reaction indices (Figure 1b) show that H_2 yield at zero time diminishes for high O/C ratios due to partial oxidation reactions of bio-oil oxygenates and H_2 . Nevertheless, the catalyst stability is noticeably improved for high O/C ratio, so that H_2 yield remains constant (0.6) for almost 3 h with O/C=0.5.

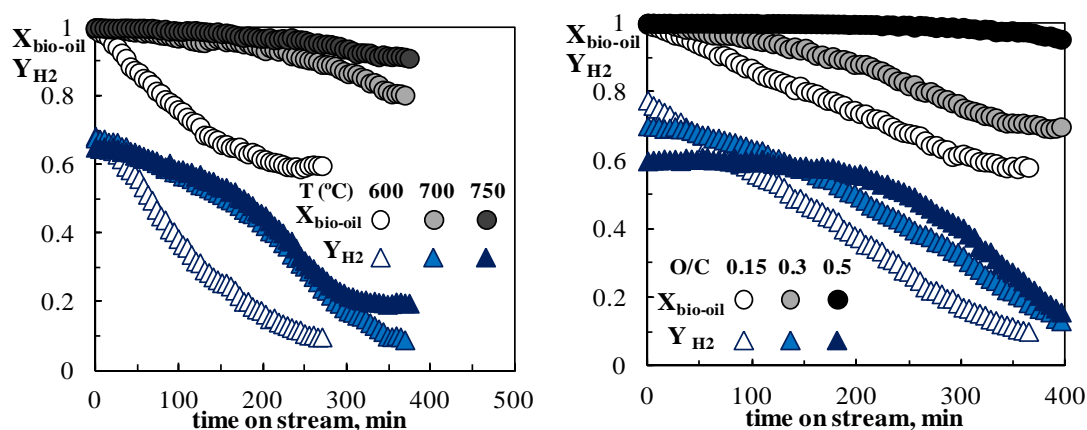


Figure 1. Effect of temperature (a) and O/C ratio (b) on bio-oil conversion and H_2 yield in OSR of bio-oil with CP33 catalyst. Reaction conditions: S/C = 6, W/F₀ = 0.15 g_{catalyst}/h/g_{bio-oil}, O/C=0.5 (graph a); 700 °C (graph b).

No reduction peaks are observed in the TPR analysis of the deactivated catalysts, which proves that Ni oxidation is not a deactivation cause. However, XRD diffractograms of catalysts deactivated at several temperatures reveal a slight increase of Ni^0 crystal size, which points out the Ni sintering as a deactivation cause, mainly at 750 °C. TPO analyses have shown higher carbon deposition rate at low temperature and O/C ratio, which is coherent with the lower deactivation rate observed under these conditions. Temperature also affects the nature of the coke, which burns at lower temperature as reforming temperature is decreased.

4. Conclusions

The H_2 yield at zero time is not significantly affected by temperature but it decreases noticeably with the increase in O/C ratio. The main deactivation cause of a NiAl_2O_4 catalyst in OSR of raw bio-oil is coke deposition (mainly encapsulating coke) and, to a lesser extent, Ni sintering. In this process, 700 °C is the optimum temperature for maximizing bio-oil conversion and H_2 yield with high catalyst stability, due to a good balance between coke deposition and Ni sintering. An intermediate O/C ratio of 0.3 is the most suitable to achieve the best balance between hydrogen yield, catalyst stability and energy requirement.

References

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Keywords

“Bio-oil”, “Oxidative steam reforming”, “Hydrogen production”, “Ni spinel catalyst”