**Optimal conditions of dolomite pre-reforming step for enhancing catalyst stability in the steam reforming of raw bio-oil**

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**Highlights**

* Dolomite activity depends highly on temperature and changes composition of raw bio-oil
* H2 yield is enhanced at 400 ºC due to conversion of acids and levoglucosan into ketones
* Severe pre-reforming conditions lead to alkyl-phenols formation and faster deactivation

**1. Introduction**

Steam reforming (SR) of the bio-oil produced by fast pyrolysis of biomass is an interesting route for renewable and sustainable production of hydrogen [1]. However, direct valorization of raw bio-oil is hampered by its complex composition, high corrosivity and thermal instability. Poly-substituted phenols (e.g., catechols, guaiacols, syringols) are the main undesired components in bio-oil, which undergo condensation reactions leading to the formation of carbonaceous material, which may cause clogging of the reactor and severe catalyst deactivation [2]. Several Ni-based catalysts have been tested under a wide range of operating conditions, which despite achieving high yields of H2 undergo a rapid deactivation. Selection of operating conditions and strategies that minimize catalyst deactivation is essential for the industrial feasibility of raw bio-oil SR. The on line two-step (thermal-catalytic) reaction system has proved to be effective for attenuating deactivation [3], and the use of dolomite as a pre-reforming catalyst has been addressed as a low-cost way of protecting the more expensive reforming catalysts [4].

In this work, the influence that temperature and dolomite space-time has on the subsequent reforming step has been studied with the aim of establishing optimal pre-reforming conditions with dolomite for enhancing H2 production and attenuating deactivation.

**2. Methods**

Raw bio-oil (obtained by fast pyrolysis of pine sawdust) was continuously fed (0.1 ml/min) into the first thermal/pre-reforming unit (Pre-SR) where the previously calcined dolomite (at 850 ºC for 5h) was located in a fixed bed reactor. The resulting volatile stream entered the fluidized bed reforming reactor (SR), where a Ni-spinel catalyst (NiAl2O4 with 33 wt % Ni) was located. The pre-reforming step was studied at 400-700 ºC and two values of space-time (1.4 and 2.8 gdolomiteh/gbio-oil), whereas conditions for steam reforming were settled at 700 ºC and 0.15 gcatalysth/gbio-oil. Additional water was co-fed with bio-oil to have a steam-to-carbon ratio (S/C) of 3. Product stream was analyzed by on-line GC and GC/MS of the liquids collected at the outlet of the Pre-SR and SR reactors. The coke deposited on the NiAl2O4 catalyst was quantified by temperature-programmed oxidation (TPO).

**3. Results and discussion**

The effect of pre-reforming (Pre-SR) on the evolution with time on stream of the overall H2 yield is studied in Figure 1, where the results are also compared with that obtained without dolomite in the first unit (black circles) and those corresponding to the Pre-SR unit outlet (dotted lines). For the same amount of dolomite (Figure 1a), the NiAl2O4 catalyst stability was enhanced when the pre-reforming was performed at 400 ºC. Figure 1b also revealed that half the amount of dolomite was necessary to improve H2 production (compared to the conventional SR) when the pre-SR was conducted at 700 ºC. The faster catalyst deactivation observed as the pre-reforming temperature was raised from 400 to 700 ºC was attributed to a higher coke deposition (from 4 to 18 wt %).



**Figure 1.** Effect of pre-reforming (Pre-SR) temperature (Graph a, 2.8 gdolomiteh/gbio-oil) and dolomite space-time (Graph b, 700 ºC) on the overall hydrogen yield. Conditions on the steam reforming (SR) step: 700 ºC, 0.15 gcatalysth/gbio-oil.

These results were explained by differences in the composition of the oxygenated stream caused by the dolomite activity for ketonization, steam reforming, WGS, cracking and H2 transfer reactions, whose relative prevalence depends on the operating conditions [5]. At 400 ºC, acids and levoglucosan were mainly converted *via* ketonization leading to acetone, 2-butanone and cyclic ketones as majority compounds. Dolomite activity for reforming reactions was favored by temperature and space-time, although cracking and hydrodeoxygenation of poly-substituted phenols were also promoted, resulting in oxygenated stream with alkyl-phenols and aromatics as majority compounds.

**4. Conclusions**

The pre-reforming with dolomite at low temperature (400 ºC) or low space-time is effective to attenuate the deactivation by coke of the Ni-spinel catalyst in the reforming step, due to the conversion of acids and levoglucosan contained in raw bio-oil into ketones, whereas more severe pre-reforming conditions promote formation of alkyl-phenols that cause faster deactivation.

**References**

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