



Full Length Article

Steam reforming of phenol as biomass tar model compound over Ni/Al₂O₃ catalyst



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HIGHLIGHTS

- Efficient Ni/Al₂O₃ catalyst (10 wt% of Ni) for the steam reforming of phenol.
- High carbon conversion (81%) using 1.5 g of catalyst at 750 °C for 60 min.
- High H₂ potential (59%) using 1.5 g of catalyst at 750 °C for 60 min.
- An increase in temperature decreases carbon deposition on the catalyst.
- High temperature (800 °C) causes catalyst deactivation by sintering.

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ABSTRACT

Catalytic steam reforming of phenol over Ni/Al₂O₃ catalyst with 10 wt% of Ni loading was carried out in a fixed bed reactor. The effect of temperature (650–800 °C), reaction time (20–80 min) and catalyst amount (0–2 g corresponding to 0–4.5 g_{cat} h g_{phenol}⁻¹) on carbon conversion, H₂ potential and catalyst deactivation was studied. High efficiency of Ni/Al₂O₃ catalyst in steam reforming of phenol is observed at 750 °C for a reaction time of 60 min when 1.5 g of catalyst (3.4 g_{cat} h g_{phenol}⁻¹) is used, with carbon conversion and H₂ potential being 81 and 59%, respectively. An increase in temperature enhances phenol reforming reaction as well as coke gasification, minimizing its deposition over the catalyst. However, at high temperatures (800 °C) an increase in Ni crystal size is observed indicating catalyst irreversible deactivation by sintering. As catalyst time on stream is increased the coke amount deposited over the catalyst increases, but no differences in Ni crystal size are observed. An increase in catalyst amount from 0 to 1.5 g increases H₂ potential, but no further improvement is observed above 1.5 g. It is not observed significant catalyst deactivation by coke deposition, with the coke amount deposited over the catalyst being lower than 5% in all the runs.

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1. Introduction

Biomass is considered as a potential renewable energy source in order to decrease our current dependence on fossil fuels [1,2]. Its abundance, renewability, carbon-neutrality and low sulphur content make biomass especially interesting to replace fossil fuels as energy source [3,4]. Among the different technologies, gasification is a promising one in which biomass is converted into a syngas stream that can be combusted in an internal combustion engine for power generation or in a furnace for heat generation [5,6]. Besides, the syngas produced can be used as a raw material for pro-

duction of fuels and chemicals by Fischer-Tropsch synthesis method [7].

The main drawback of biomass gasification process and its large scale implementation is the formation of unwanted byproducts together with syngas, such as particulates, alkali metals, fuel-bound nitrogen, sulphur, chlorine and tar [7,8]. These byproducts cause several problems in process equipment (corrosion, clogging...) as well as environmental pollution. Tar is a complex mixture of condensable hydrocarbons with molecular weight higher than benzene and its elimination has raised significant concern in literature [3,5,8–10]. The concentration and the composition of the tar in the gas stream produced in biomass gasification depend on the raw material, the operating conditions and the gasification technology used [11]. Tar lead to several operational problems in process equipment, such as metal corrosion, clogging filters and

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valves or condensing in cold spots plugging them. Besides, tar concentration limits the application of the produced syngas in internal combustion engines ($<100 \text{ mg/Nm}^3$) as well as gas turbines ($<5 \text{ mg/Nm}^3$) due to the clogging of pipelines and injectors in engines and turbines [8]. Furthermore, tar compounds make the produced gas useless for applications such as Fischer-Tropsch process for chemical production, in which tar presence leads to serious coke deposition over the catalyst.

Tar removal methods can be classified in primary and secondary methods, where the gas cleaning treatment is carried out inside or downstream the gasifier respectively [10,12]. Several technologies have been studied for a downstream tar removal, generally divided into physical methods, catalytic cracking or thermal treatment [8]. Among them, downstream catalytic steam reforming is widely studied in order to convert tar compounds into useful fuel gas, thus obtaining high purity gas and increasing fuel value. Natural minerals, such as natural calcite, olivine and dolomite [13–16], nickel based catalyst [11,17,18] or non-nickel metal catalyst [4] have been extensively studied in order to find a catalyst that is inexpensive, effective in tar reduction, resistant to deactivation and easily regenerated.

Tar model compounds are widely used in order to deeply study the catalyst performance and the process operating conditions. Toluene, benzene, naphthalene and phenol are usually identified as the principal biomass gasification tar model compounds [3] and they are the commonly chosen tar model compounds to study its steam reforming over supported metal catalysts [4,19–22]. Ni commercial steam reforming catalyst has been widely studied for biomass tar reforming [8,11], given that it allows obtaining high tar conversion and improving the quality of the syngas, since light hydrocarbons are also reformed and higher H_2 yields are obtained. Besides, several supports (Al_2O_3 , SiO_2 , ZrO_2 , MgO , olivine...) [20,23–25] and promoters (CeO_2 , Co , La ...) [22,26] for Ni metal have been studied in the literature in order to improve the activity, stability, coking resistance and regenerability of the catalyst.

In this work phenol has been used as a model compound of biomass gasification tar, given that it is an oxygenated aromatic compound that is more refractory to reforming than non-aromatic compounds and causes faster deactivation than non-oxygenated compounds. Phenol steam reforming over $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst has been studied in order to optimize the experimental conditions (temperature, reaction time, catalyst amount) for maximizing the phenol conversion and minimizing the catalyst deactivation by coke deposition as well as sintering. This study has been conducted with the aim of optimizing operating conditions for a future detailed study of the steam reforming process in which different model compounds or catalysts will be assayed. It should be noted that steam reforming of phenol over Ni metal catalyst has also been studied in order to obtain information about bio-oil steam reforming considering phenol as bio-oil model compound [27,28].

2. Experimental

2.1. Catalyst preparation and characterization

A nickel alumina catalyst ($\text{Ni}/\text{Al}_2\text{O}_3$) with a nickel loading of 10 wt% was prepared by a simple impregnation method, and tested in the catalytic steam reforming of phenol. Approximately 11 g of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich) were dissolved in 20 ml of deionised water and mixed with approximately 20 g of aluminium oxide ($\gamma\text{-Al}_2\text{O}_3$, 96% Alfa Aesar). The precursor was stirred at 100°C for around 30 min to ensure homogeneous mixture of components and promote water evaporation. Subsequently, the resulting semi-solid mixture was further dried overnight at 105°C , and calcined at 750°C with $20^\circ\text{C min}^{-1}$

heating rate in an air atmosphere for 3 h. The resulting catalyst was crushed and sieved to obtain finer particles with a size in the 0.18–0.24 mm range. The prepared catalyst was not reduced, since during the process some of the pyrolysis gases, such as H_2 and CO , have the capability to reduce the catalyst itself [29].

The physical or structural properties of the catalyst (BET surface area, pore volume and pore size distribution) were measured using Micromeritics TriStar 3000. These properties were determined by the adsorption-desorption of N_2 at -192°C . The experimental procedure consists in degassing the sample for approximately 8 h at 150°C to remove all possible impurities, followed by adsorption-desorption of N_2 . The surface area was calculated using the BET method and the average pore diameter was calculated using the BJH method, with the calculated values being $116.5 \text{ m}^2/\text{g}$ and 24 \AA , respectively.

X-ray diffraction (XRD) analyses of the catalyst were carried out using Bruker D8 instrument with a $\text{CuK}\alpha$ radiation for a qualitative phase analysis (fresh catalyst) and crystal size determination (used catalyst). The samples were ground to less than $75 \mu\text{m}$ size and loaded into the 20 mm aperture of an aluminium sample holder. Concerning the fresh catalyst, 3 different phases corresponding to NiO , Al_2O_3 and NiAl_2O_4 have been identified. The determinations of Ni crystal size for used catalysts were carried out using Scherrer equation.

Temperature programmed oxidation (TPO) of used catalysts were carried out to determine the amount and nature of the coke deposited over the catalyst for which the thermogravimetric analyzer Shimadzu TGA-50 was used. About 20 mg of sample was heated in air atmosphere at $15^\circ\text{C min}^{-1}$ to a final temperature of 800°C and maintained for 10 min at this temperature. Besides, high resolution scanning electron microscopy (SEM, Hitachi SU8230) was used to identify the nature of the coke deposited over the catalyst.

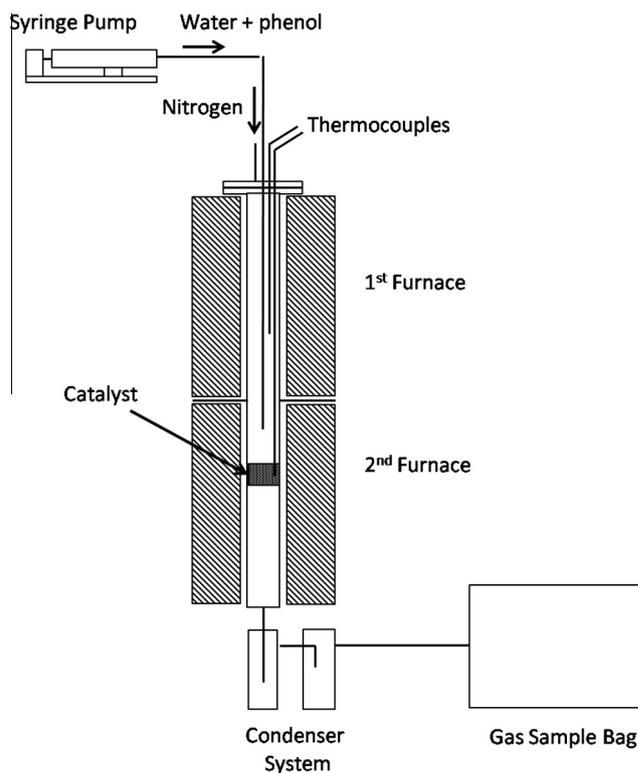


Fig. 1. Experimental equipment used for steam reforming of phenol.

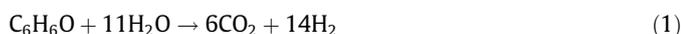
2.2. Experimental equipment and procedure

Fig. 1 shows the experimental equipment used to study the steam reforming of phenol over Ni/Al₂O₃ catalyst with 10 wt% of Ni loading. Phenol was dissolved in water at a steam/carbon molar ratio of 13, and they were fed continuously by means of a syringe pump using a flow rate of 6.64 ml min⁻¹. The first furnace was maintained at 250 °C to evaporate the feedstock before entering the second reactor. Besides, 80 ml min⁻¹ of nitrogen was fed to sweep the volatiles formed in the reactor. Both reactors were 16 cm length with an internal diameter of 2.2 cm and each was separately heated externally by an electrical furnace. The influence of the reforming reactor temperature was studied in the 650–800 °C range, using 1 g of Ni/Al₂O₃ catalyst for a reaction time of 40 min. As aforementioned, the catalyst has not been reduced before use because H₂ and CO are present in the reaction medium and, as concluded in a previous work [30], they are capable of reducing the catalyst. Therefore, the effect of the reaction time (20–80 min) was studied to analyze the evolution of catalyst activity by using 1 g of Ni/Al₂O₃ at a reforming temperature of 750 °C. Moreover, the influence of the catalyst amount on phenol conversion was analyzed in the 0–2 g range (corresponding to space-times in the 0–4.5 g_{cat} h g_{phenol}⁻¹ range) at 750 °C for 60 min.

The volatile stream formed goes to a condensation system which is formed by two condensers cooled with dry-ice. The non-condensable gases are collected in a 10 L Teldar™ gas sample bag. The gases are collected for 20 min subsequent to the end of each run to ensure that all the produced gases are collected. The gases collected in the gas sample bag were analyzed off-line by gas chromatography. Hydrocarbon gases (from C₁ to C₄) were determined by a Varian 3380 chromatograph with a flame ionisation detector (GC/FID), 80–100 mesh Hysep column and using nitrogen as carrier gas. Permanent gases, i.e., CO, O₂, N₂ and H₂, were determined by a Varian 3380 chromatograph with a 60–80 mesh molecular sieve column and argon as carrier gas with a thermal conductivity detector, whereas CO₂ was analyzed by another Varian 3380 GC provided with a Hysep 80–100 mesh column and using argon as carrier gas and a thermal conductivity detector.

The condensers were weighed before and after each run to measure the liquid amount obtained and N₂ was used as internal standard to calculate the gas yield. Each run was repeated at least twice to verify the reproducibility of the results and the mass balance closure was between 95 and 105% in all the runs.

The overall reaction of catalytic steam reforming of phenol is defined as follows:



In order to analyze the effect of operating conditions on the steam reforming of phenol, carbon conversion and H₂ potential was defined. The carbon conversion was defined as the moles of carbon in the gaseous products divided by the moles of carbon fed and H₂ potential as percentage of the potential stoichiometric H₂ yield, where stoichiometric H₂ moles were calculated according to Eq. (1).

$$\text{C conversion (\%)} = \frac{\text{moles of carbon in the product gas}}{\text{moles of carbon in the feed}} 100 \quad (2)$$

$$\text{H}_2 \text{ potential} = \frac{\text{moles of H}_2 \text{ in the product gas}}{\text{moles of H}_2 \text{ in stoichiometric potential}} 100 \quad (3)$$

The yield of gas compounds was calculated as follows,

$$\text{Yield (\%)} = \frac{\text{g of the compound in the product gas}}{\text{g of phenol fed}} 100 \quad (4)$$

3. Results

3.1. Effect of temperature

Fig. 2 shows the effect of temperature on carbon conversion and H₂ potential obtained in the steam reforming of phenol over Ni/Al₂O₃ catalyst (1 g of catalyst corresponding to a space time of 2.25 g_{cat} h g_{phenol}⁻¹). It can be seen that temperature has great influence on phenol reforming, increasing the carbon conversion from 8% at 650 °C to 57% at 800 °C. Likewise, H₂ potential increases as reforming temperature is increased, reaching a value of 47% at 800 °C. This increase in carbon conversion and H₂ potential can be attributed to the endothermic nature of oxygenated compound reforming reaction, which is enhanced as temperature is increased.

The same trend of carbon conversion and H₂ potential with temperature was observed in the literature on steam reforming of phenol over Ni/Al₂O₃ catalyst [28,31]. Wang et al. [28] studied the steam reforming of different bio-oil model compounds, in which phenol has been identified as the most refractory compound due to its stable structure with an aromatic ring.

Fig. 3 displays the effect of temperature on the yield of the gas compounds. It can be seen that an increase in temperature increases the yield of all gas compounds due to the enhancement of reforming reaction, reaching a maximum CO₂, CO and H₂ yield at 800 °C, 66, 55 and 14 wt%, respectively. Phenol steam reforming reaction on nickel surface is explained by two possible mechanisms [32], which are initiated with the dissociation of O–H followed by: (i) a ring opening caused by C–H scission and C=C rupture in positions 2 and 6; (ii) C–O bond dissociation followed by C–H and C=C rupture. Both decomposition mechanisms give way to H₂, CO and light hydrocarbon formation. The low values of light hydrocarbon yields obtained (lower than 1 wt% in all the temperature range studied) shows that its reforming is almost complete even at low temperatures. The low CH₄ yield obtained can be attributed to the absence of methyl group in the phenol structure.

Nevertheless, it can be observed that the ratio between CO and CO₂ is significantly changed as temperature is increased, showing that an increase in temperature increases the phenol reforming reaction and causes thermodynamic equilibrium displacement in the water gas shift exothermic reaction.

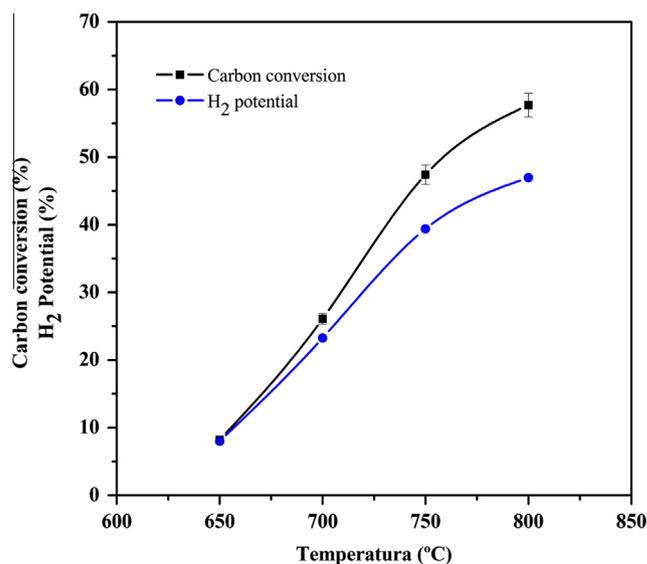


Fig. 2. Effect of temperature on carbon conversion and H₂ potential (40 min; 1 g of catalyst).

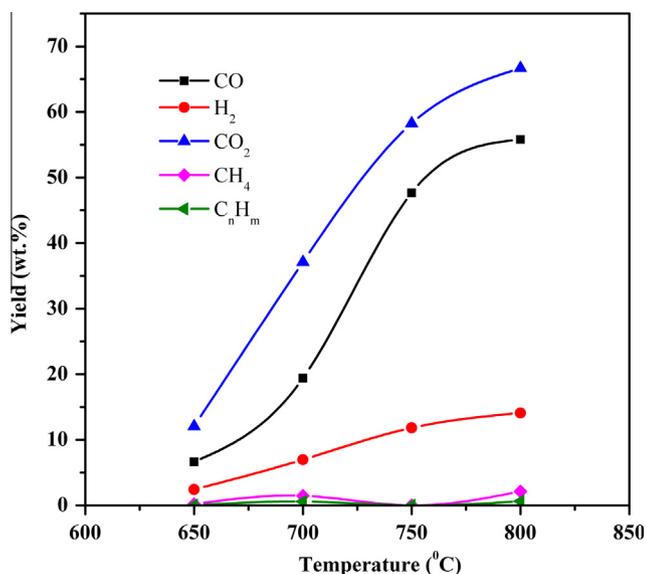


Fig. 3. Effect of temperature on gas compounds yield (40 min; 1 g of catalyst).

Fig. 4 shows the temperature programmed oxidation (DTG-TPO) curves for the coke deposited over Ni/Al₂O₃ catalyst used in the steam reforming of phenol at different temperatures. Ni/Al₂O₃ catalyst deactivation by coke deposition has been widely studied in the literature [33,34] for which two types of coke have been identified: (i) amorphous coke, which is burnt at low temperatures (around 450 °C) since its combustion is activated by Ni metal on which the coke is deposited causing its encapsulation; (ii) filamentous coke, which is not adsorbed over Ni sites and it is combusted at high temperatures (above 450 °C).

The coke deposited over the catalyst used at 650 °C (4.6 wt%) is combusted in a wide temperature range, between 350 and 600 °C. Although a main peak at 480 °C is observed, several shoulders can be observed at different temperatures (370, 410 and 460 °C), which evidence the heterogeneous nature of the coke deposited. This heterogeneity reveals the existence of nascent coke (the shoulder at 370 °C), which is formed by phenol condensation and adsorbed

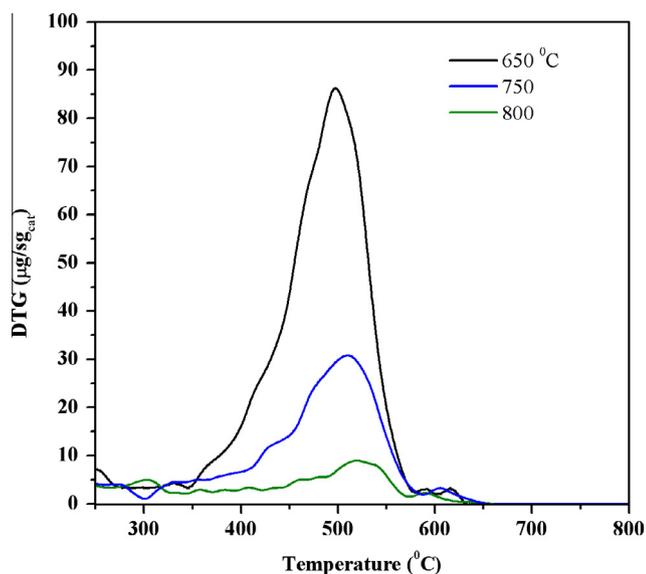


Fig. 4. DTG-TPO curves of the coke deposited over the catalyst used at different temperatures (40 min; 1 g of catalyst).

as phenate species over Ni sites [35] and its combustion is catalyzed by Ni metal sites. This coke evolves into more condensate structures by multilayer growing and it is separated progressively from Ni sites, requiring higher temperatures for its combustion.

Furthermore, the composition of the coke deposited in steam reforming depends on the operating conditions used (temperature, steam/carbon ratio and space-time) since coke deposition is a result of a balance between its formation and its elimination by gasification [36]. Consequently, the coke deposited at 750 °C is significantly affected by gasification, which is faster for the less condensed coke. Thus, at 750 °C the coke amount deposited is lower (2.1 wt%) and more evolved, with the peak being moved at higher temperatures. Coke gasification rate is higher at 800 °C, decreasing the amount of coke deposited until 1.1 wt%.

Fig. 5 shows SEM images for the fresh (a) and used catalyst (at 650 (b), 750 (c) and 800 (d)). It can be seen that SEM images do not show the presence of high structured filamentous coke. It should be noted that the catalyst with the highest coke amount is that used at the lowest temperature, for which an amorphous coke deposited between catalyst particles is observed.

XRD analysis for the catalyst used in the reforming of phenol at 650 °C, 750 °C and 800 °C have been carried out in order to study the influence of the reforming temperature on the Ni crystal size. The catalyst used at 650 °C does not present a peak representative of Ni metal, indicating that 650 °C is not high enough to reduce the catalyst. The catalyst used at 750 °C presents a peak representative of the Ni metal with a crystal size of 45 Å. Likewise, for the catalyst used at 800 °C a peak characteristic of Ni metal is observed with a crystal size of 72 Å, showing that reforming temperature causes catalyst irreversible deactivation by Ni metal sinterization.

3.2. Effect of time on stream

Fig. 6 displays the effect of reaction time on carbon conversion and H₂ potential obtained in the catalytic reforming of phenol over Ni/Al₂O₃ catalyst at 750 °C (1 g of catalyst corresponding to a space time of 2.25 g_{cat} h g_{phenol}⁻¹). It can be seen that an increase in time on stream until 60 min gives way to a linear increase in carbon conversion, increasing from 35% for 20 min to 56% for 60 min. Above 60 min no change in carbon conversion is observed. As aforementioned, the catalyst is not reduced before use because H₂ and CO present in the reaction medium will reduce it [37]. It can be seen that an initial period of catalyst activation is necessary and the catalyst is reduced completely for the run carried out for 60 min, maintaining its activity above this reaction time. Similarly, H₂ potential increases as time on stream increased, reaching a maximum value of 39% for the run carried out for 40 min and maintaining this value for longer reaction times.

Fig. 7 shows the effect of reaction time in the catalytic reforming of phenol over Ni/Al₂O₃ catalyst at 750 °C on the individual gas compounds yields obtained. It can be seen that an increase in reaction time until 40 min gives way to an increase in CO, CO₂ and H₂ yield (47, 58, 11%) due to the enhancement of reforming reaction as the catalyst is reduced. An increase in reaction time from 40 to 60 min shows a significant increase in CO₂ yield (from 58% to 73%) and a slight increase in H₂ yield (from 11% to 12%). However, an increase in reaction time from 60 to 80 min gives way to a decrease in CO₂ (from 73% to 63%) and H₂ yield (from 12% to 11%), but an increase in the yield of CO (from 49% to 57%). The trend observed can be attributed to water gas shift reaction, which is enhanced when time on stream increases from 40 to 60 min due to the complete reduction of the catalyst and an increase in its activity. However, it seems that an increase in reaction time above 60 min reduces the catalyst activity for water gas shift reaction since coke deposition over the catalyst decrease its activity for this reaction.

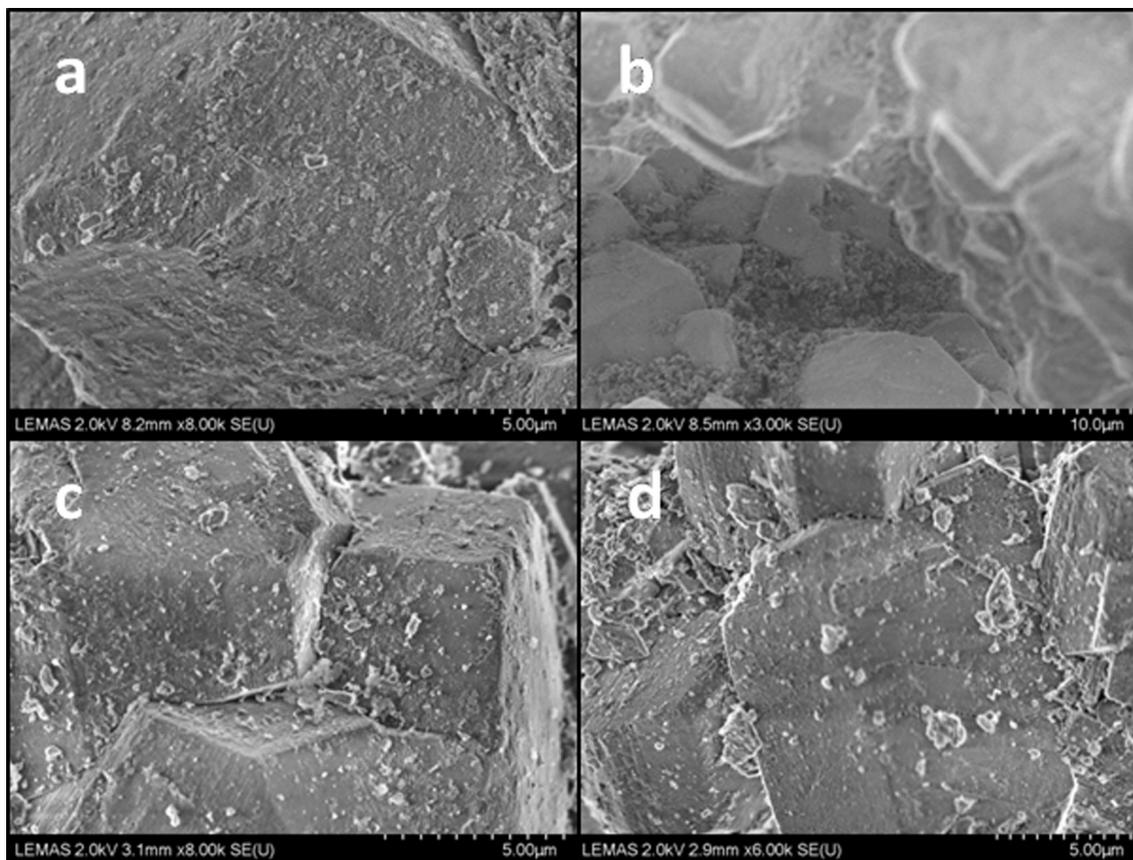


Fig. 5. SEM imagines of the fresh catalyst (a) and used catalyst at 650 (b), 750 (c) and 800 °C (d) (40 min; 1 g of catalyst).

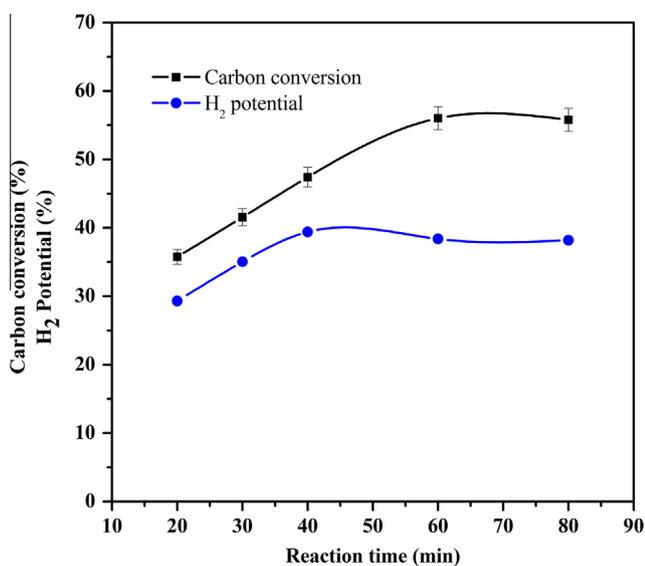


Fig. 6. Effect of reaction time on carbon conversion and H₂ potential (750 °C; 1 g of catalyst).

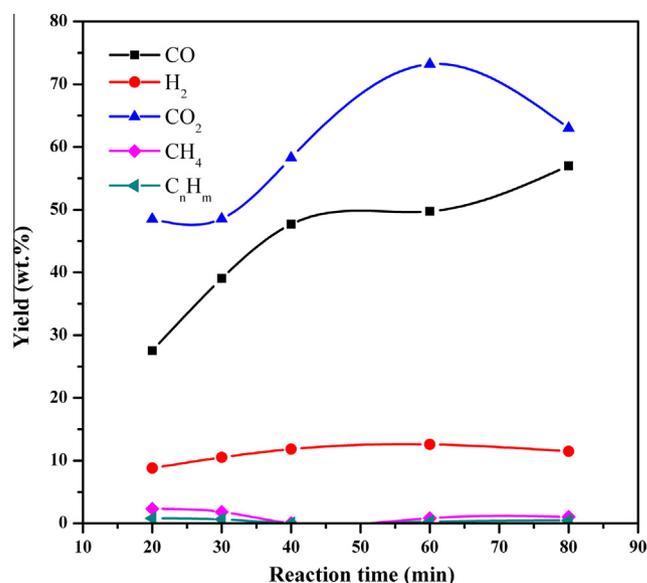


Fig. 7. Effect of reaction time on gas compounds yield (750 °C; 1 g of catalyst).

DTG-TPO results for the Ni/Al₂O₃ catalyst used in phenol steam reforming at 750 °C for different reaction times (Fig. 8) show that the coke amount increases as reaction time is increased, from 2.1% for 20 min to 3.8% for 80 min. It can be seen that the coke deposited over all the catalysts studied is combusted between 350 and 600 °C and they present a prevailing peak around 500 °C. Nevertheless, the nature of the coke deposited over the

catalyst is different depending on the reaction time. The catalyst used for 60 min presents a significant shoulder at low temperatures (400 °C) and a main peak at intermediate temperatures (500 °C). Although the coke amount does not increase significantly, an increase in reaction time until 80 min gives way to a higher degree of structuring of the carbonaceous material deposited, which decreases the shoulder at low temperatures

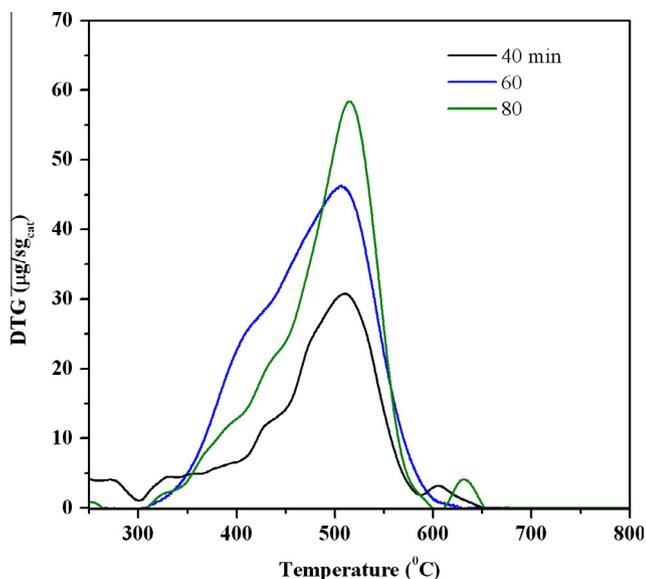


Fig. 8. DTG-TPO curves of the coke deposited over the catalyst used for different reaction times (750 °C; 1 g of catalyst).

(400 °C) and increases the main peak at higher temperatures (500 °C).

SEM analysis for the fresh (Fig. 9a) and the catalyst used for different reaction times, 40 (Fig. 9b), 60 (Fig. 9c) and 80 min (Fig. 9d), have been carried out in order to gain knowledge about the coke nature and position. Regarding the SEM images, no significant differences are observed for low times on stream due to the low coke

amount deposited over the catalyst. However, for long reaction times (Fig. 11d), an amorphous coke deposited is clearly observed over catalyst particles. XRD analysis has also been used to calculate the Ni crystal size and analyze the influence of the reaction time over catalyst deactivation by sintering. The catalysts used for 40, 60 and 80 min have been analyzed and no influence of reaction time over catalyst sinterization is observed, with the Ni crystal size being around 45 Å for all the catalysts studied. This evidences that there is no Ni particle dragging, which is consistent with the absence of filamentous coke.

3.3. Effect of catalyst amount

Fig. 10 displays the effect of the catalyst amount used (0, 1, 1.5 and 2 g of catalyst corresponding to space times of 0, 2.25, 3.4 and 4.5 $\text{g}_{\text{cat}} \text{h g}_{\text{phenol}}^{-1}$) on carbon conversion and H_2 yield obtained at 750 °C and for a reaction time of 60 min (a steam/carbon molar ratio of 13 and a flowrate of 6.64 ml min^{-1}). The run without catalyst was carried out using 1 g of sand. As observed, the catalyst used is highly efficient, given that it increases carbon conversion from 9 to 56% and H_2 potential from 4 to 38% when 1 g of catalyst is added. An increase in the catalyst amount used from 1 to 1.5 g leads to a significant increase in carbon conversion as well as H_2 potential, reaching values of 81 and 59%, respectively. However, an increase in catalyst amount above 1.5 g does not show a notable influence in phenol reforming, maintaining carbon conversion and H_2 potential almost constant when catalyst amount is increased to 2 g. Wang et al. [28] obtained similar results studying the steam reforming of bio-oil model compounds over Ni/ Al_2O_3 catalyst.

Fig. 11 shows that an increase in catalyst amount from 0 to 1.5 g gives way to a increase in the yield of CO , CO_2 and H_2 from 10, 9.9

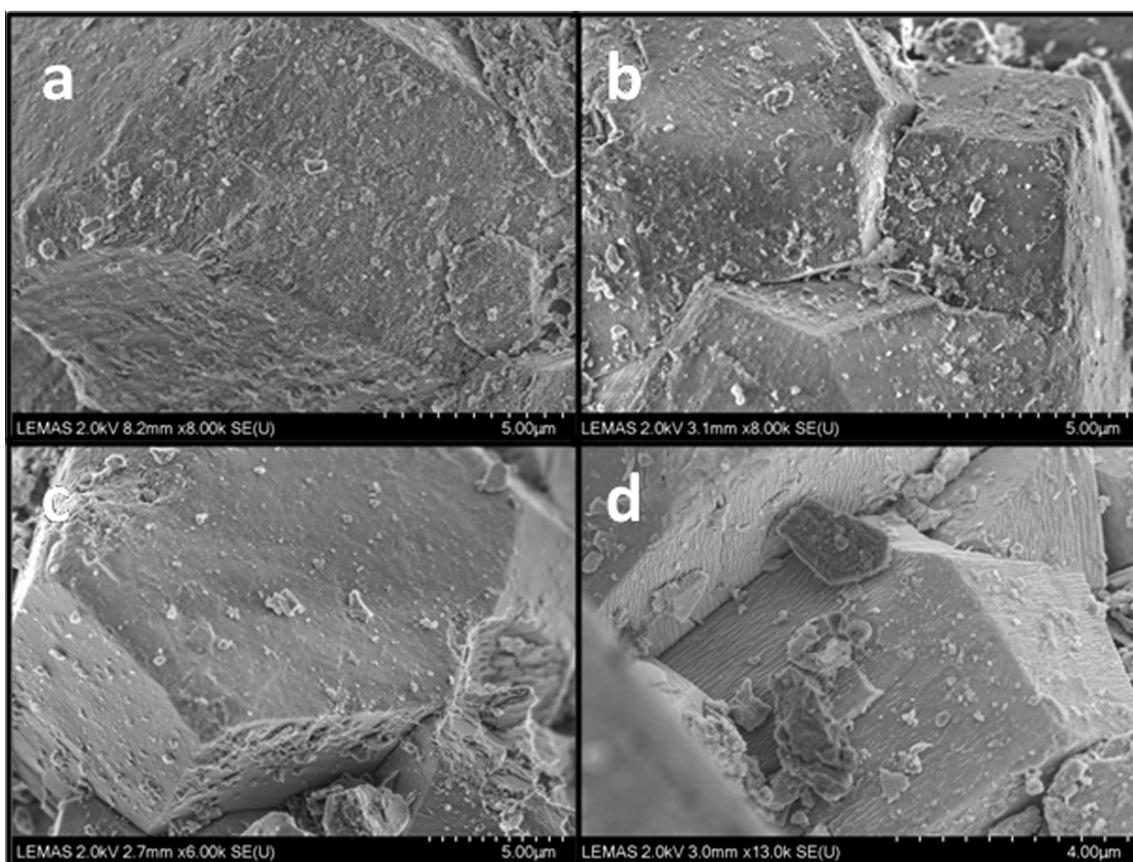


Fig. 9. SEM images of the fresh catalyst (a) and used catalyst for 40 (b), 60 (c) and 80 (d) min (750 °C; 1 g of catalyst).

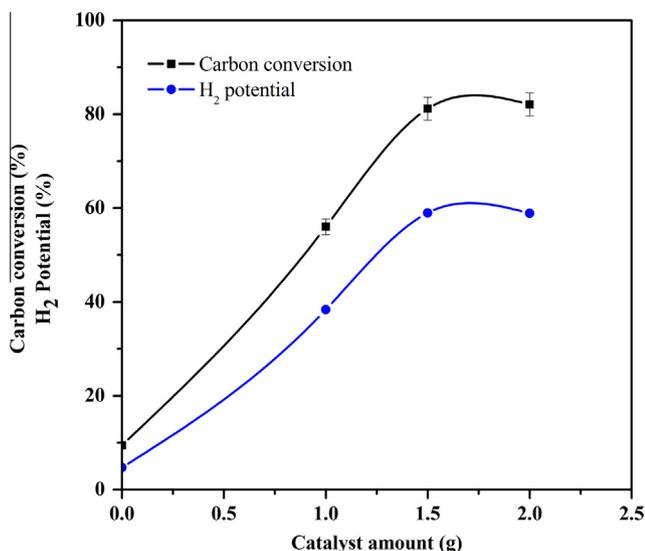


Fig. 10. Effect of catalyst amount on carbon conversion and H₂ potential (750 °C; 60 min).

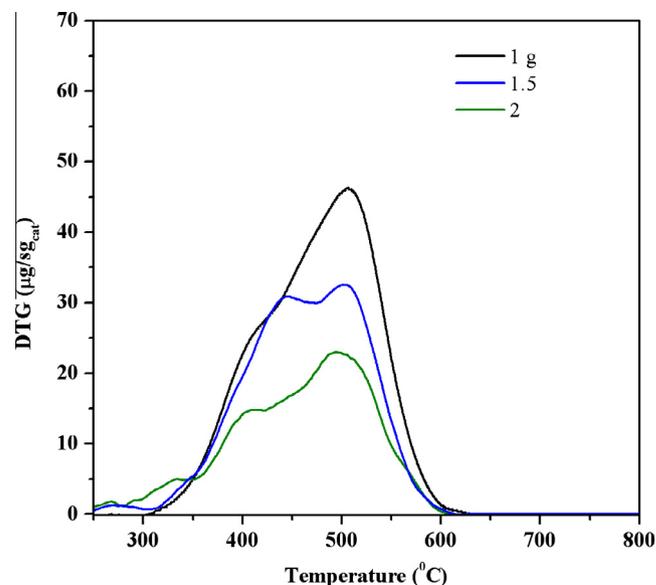


Fig. 12. DTG-TPO curves of the coke deposited over the catalyst used for different catalyst amounts (750 °C; 60 min).

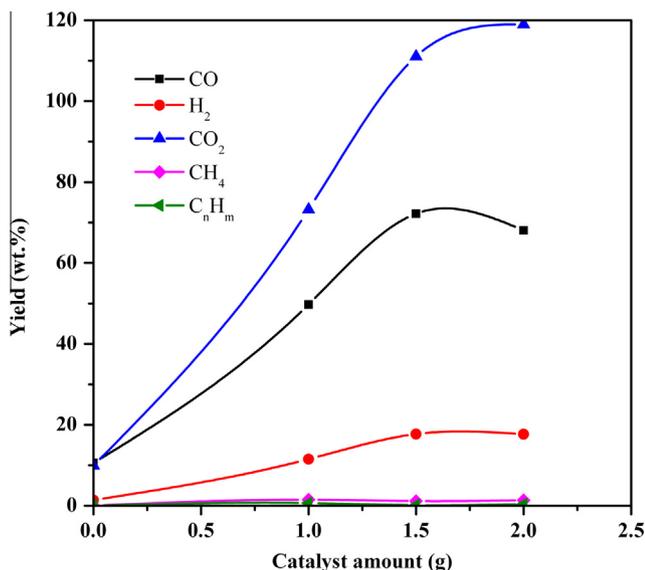


Fig. 11. Effect of catalyst amount on gas compounds yield (750 °C; 60 min).

and 1.4 wt% to 72, 111 and 17 wt%, respectively. However, an increase in space-time above this value lead to an increase in the yield of CO₂ (118 wt%) and a decrease in the yield of CO (68 wt %), indicating that water gas shift reaction is favoured when a large amount of catalyst is used. Swierczynski et al. [38] have also seen the enhancement of water gas shift reaction when space-time is increased. They study toluene steam reforming over Ni/olivine catalyst at 800 and 650 °C showing that an increase in space-time led to an increase in CO₂ selectivity and a decrease in CO selectivity.

Fig. 12 displays TPO curves of the coke deposited over Ni/Al₂O₃ catalyst in the steam reforming of phenol when different amounts of catalyst are used at 750 °C for 60 min. It can be observed that the amount of catalyst used does not affect significantly the nature of the coke deposited but it does the amount of coke deposited over the catalyst. All the TPO curves present a main peak at 500 °C with a shoulder at 400 °C which evidences that the coke deposited over the catalyst has a similar degree of graphitization and similar loca-

tion over the catalyst. Furthermore, as the amount of catalyst (catalytic bed length) is increased, the amount of coke deposited on the catalyst decreases. Consequently, based on the evolution of phenol concentration with catalyst amount, the role of phenol should be noted as coke precursor by phenate species adsorbed as intermediates [35].

4. Conclusion

High carbon conversion and H₂ potential has been obtained in the steam reforming of phenol over Ni/Al₂O₃ catalyst, reaching a value of 81 and 59%, respectively, at 750 °C for a reaction time of 60 min and using 1.5 g of catalyst. The coke deposited over the catalyst is mainly of low degree of graphitization and its amount has been lower than 5% in the whole operating range studied.

An increase in temperature gives way to an increase in carbon conversion and H₂ potential due to the enhancement of phenol reforming reaction. Besides, coke gasification rate increases as temperature is increased, and the amount of coke deposited over the catalyst significantly decreases (from 4.6% to 1.1%) when temperature is increased from 650 to 800 °C. However, a high reforming temperature (800 °C) causes an increase in Ni crystal size and, therefore, catalyst deactivation by sintering.

It is concluded that an initial period of NiO reduction is required to activate the catalyst. Thus, an increase in time on stream increases the carbon conversion and H₂ potential until 60 min of time on stream, from which the catalyst activity is maintained constant. Regarding coke deposition, an increase in time on stream influences the amount of coke deposited but also the nature of the coke, whose amount and graphitization degree is higher as reaction time increases.

The amount of the catalyst used has great influence on phenol steam reforming, with carbon conversion increasing linearly, as well as H₂ potential, with the amount of catalyst used. However, phenol conversion seems to have a ceiling value in the steam reforming, whereas a further enhancement of water gas shift reaction is observed.

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References

- [1] Demirbas A. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. *Energy Convers Manage* 2008;49:2106–16.
- [2] Vassilev SV, Vassileva CG, Vassilev VS. Advantages and disadvantages of composition and properties of biomass in comparison with coal: an overview. *Fuel* 2015;158:330–50.
- [3] Shen Y, Yoshikawa K. Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis – a review. *Renew Sustain Energy Rev* 2013;21:371–92.
- [4] Li D, Tamura M, Nakagawa Y, Tomishige K. Metal catalysts for steam reforming of tar derived from the gasification of lignocellulosic biomass. *Bioresour Technol* 2015;178:53–64.
- [5] Asadullah M. Barriers of commercial power generation using biomass gasification gas: a review. *Renew Sustain Energy Rev* 2014;29:201–15.
- [6] Heidenreich S, Foscolo PU. New concepts in biomass gasification. *Prog Energy Combust Sci* 2015;46:72–95.
- [7] Choudhury HA, Chakma S, Moholkar VS. Chapter 14 – biomass gasification integrated Fischer-Tropsch synthesis: perspectives, opportunities and challenges. In: Sukumaran APBS, editor. *Recent advances in thermo-chemical conversion of biomass*. Boston: Elsevier; 2015. p. 383–435.
- [8] Anis S, Zainal ZA. Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: a review. *Renew Sustain Energy Rev* 2011;15:2355–77.
- [9] Asadullah M. Biomass gasification gas cleaning for downstream applications: a comparative critical review. *Renew Sustain Energy Rev* 2014;40:118–32.
- [10] Devi L, Ptasinaki KJ, Janssen FJJG. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenergy* 2003;24:125–40.
- [11] Chan FL, Tanksale A. Review of recent developments in Ni-based catalysts for biomass gasification. *Renew Sustain Energy Rev* 2014;38:428–38.
- [12] Goransson K, Soderlind U, He J, Zhang W. Review of syngas production via biomass DFBGs. *Renew Sustain Energy Rev* 2011;15:482–92.
- [13] Constantinou DA, Efstathiou AM. The steam reforming of phenol over natural calcite materials. *Catal Today* 2009;143:17–24.
- [14] Devi L, Ptasinaki KJ, Janssen FJJG, van Paasen SVB, Bergman PCA, Kiel JHA. Catalytic decomposition of biomass tars: use of dolomite and untreated olivine. *Renew Energy* 2005;30:565–87.
- [15] Erkiaga A, Lopez G, Amutio M, Bilbao J, Olazar M. Steam gasification of biomass in a conical spouted bed reactor with olivine and γ -alumina as primary catalysts. *Fuel Process Technol* 2013;116:292–9.
- [16] Tuomi S, Kaisalo N, Simell P, Kurkela E. Effect of pressure on tar decomposition activity of different bed materials in biomass gasification conditions. *Fuel* 2015;158:293–305.
- [17] Coll R, Salvado J, Fariol X, Montane D. Steam reforming model compounds of biomass gasification tars: conversion at different operating conditions and tendency towards coke formation. *Fuel Process Technol* 2001;74:19–31.
- [18] Li C, Hirabayashi D, Suzuki K. Development of new nickel based catalyst for biomass tar steam reforming producing H_2 -rich syngas. *Fuel Process Technol* 2009;90:790–6.
- [19] Zhang R, Wang H, Hou X. Catalytic reforming of toluene as tar model compound: effect of Ce and Ce–Mg promoter using Ni/olivine catalyst. *Chemosphere* 2014;97:40–6.
- [20] Park HJ, Park SH, Sohn JM, Park J, Jeon JK, Kim SS, et al. Steam reforming of biomass gasification tar using benzene as a model compound over various Ni supported metal oxide catalysts. *Bioresour Technol* 2010;101:S101–3.
- [21] Koike M, Ishikawa C, Li D, Wang L, Nakagawa Y, Tomishige K. Catalytic performance of manganese-promoted nickel catalysts for the steam reforming of tar from biomass pyrolysis to synthesis gas. *Fuel* 2013;103:122–9.
- [22] Bona S, Guillen P, Alcalde JG, Garcia L, Bilbao R. Toluene steam reforming using coprecipitated Ni/Al catalysts modified with lanthanum or cobalt. *Chem Eng J* 2008;137:587–97.
- [23] Laosiripojana N, Sutthisripok W, Charojrochkul S, Assabumrungrat S. Development of Ni–Fe bimetallic based catalysts for biomass tar cracking/reforming: effects of catalyst support and co-fed reactants on tar conversion characteristics. *Fuel Process Technol* 2014;127:26–32.
- [24] Michel R, Lamacz A, Krzton A, Djéga-Mariadassou G, Burg P, Courson C, et al. Steam reforming of α -methyl-naphthalene as a model tar compound over olivine and olivine supported nickel. *Fuel* 2013;109(July):653–60.
- [25] Shen Y, Chen M, Sun T, Jia J. Catalytic reforming of pyrolysis tar over metallic nickel nanoparticles embedded in pyrochar. *Fuel* 2015;159:570–9.
- [26] Ashok J, Kawi S. Steam reforming of toluene as a biomass tar model compound over Co_2 promoted Ni/CaO– Al_2O_3 catalytic systems. *Int J Hydrogen Energy* 2013;38:13938–49.
- [27] Wang S, Zhang F, Cai Q, Li X, Zhu L, Wang Q, et al. Catalytic steam reforming of bio-oil model compounds for hydrogen production over coal ash supported Ni catalyst. *Int J Hydrogen Energy* 2014;39:2018–25.
- [28] Wang S, Cai Q, Zhang F, Li X, Zhang L, Luo Z. Hydrogen production via catalytic reforming of the bio-oil model compounds: acetic acid, phenol and hydroxyacetone. *Int J Hydrogen Energy* 2014;39:18675–87.
- [29] Wu C, Williams PT. Hydrogen production by steam gasification of polypropylene with various nickel catalysts. *Appl Catal B* 2009;87:152–61.
- [30] Efica CE, Wu C, Williams PT. Syngas production from pyrolysis-catalytic steam reforming of waste biomass in a continuous screw kiln reactor. *J Anal Appl Pyrol* 2012;95:87–94.
- [31] Polychronopoulou K, Bakandritsos A, Tzitzios V, Fierro JLG, Efstathiou AM. Absorption-enhanced reforming of phenol by steam over supported Fe catalysts. *J Catal* 2006;241:132–48.
- [32] Matas Guell B, Babich IV, Lefferts L, Seshan K. Steam reforming of phenol over Ni-based catalysts – a comparative study. *Appl Catal B* 2011;106:280–6.
- [33] Wu C, Williams PT. Investigation of coke formation on Ni–Mg–Al catalyst for hydrogen production from the catalytic steam pyrolysis-gasification of polypropylene. *Appl Catal B* 2010;96:198–207.
- [34] Vicente J, Montero C, Ereña J, Azkoiti MJ, Bilbao J, Gayubo AG. Coke deactivation of Ni and Co catalysts in ethanol steam reforming at mild temperatures in a fluidized bed reactor. *Int J Hydrogen Energy* 2014;39:12586–96.
- [35] Garbarino G, Sanchez Escribano V, Finocchio E, Busca G. Steam reforming of phenol–ethanol mixture over 5% Ni/ Al_2O_3 . *Appl Catal B* 2012;113–114:281–9.
- [36] Remiro A, Valle B, Aguayo AT, Bilbao J, Gayubo AG. Operating conditions for attenuating Ni/ La_2O_3 – Al_2O_3 catalyst deactivation in the steam reforming of bio-oil aqueous fraction. *Fuel Process Technol* 2013;115:222–32.
- [37] Clause O, Gazzano M, Trifiro F, Vaccari A, Zatorski L. Preparation and thermal reactivity of nickel/chromium and nickel/aluminium hydrotalcite-type precursors. *Appl Catal* 1991;73:217–36.
- [38] Swierczynski D, Courson C, Kiennemann A. Study of steam reforming of toluene used as model compound of tar produced by biomass gasification. *Chem Eng Process Intensif* 2008;47:508–13.