

# **Process intensification by exploiting diluted 2<sup>nd</sup> Generation Bio-ethanol in the Low-Temperature Steam Reforming process**

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## **ABSTRACT**

Second generation bioethanol, obtained by the fermentation of lignocellulosic biomass, which is not competitive with the food and feed field, is one of the most interesting promising biofuels, already available in semi-commercial amount. Steam reforming of bioethanol has been used here for sustainable hydrogen and syngas production. Differently purified second generation bioethanol feeds, directly supplied by an industrial plant, for the steam reforming process, assessing the influence of impurities and catalyst formulation. Ni/La<sub>2</sub>O<sub>3</sub>, Ni/ZrO<sub>2</sub> and Ni/CaO-ZrO<sub>2</sub> prepared by Flame Spray Pyrolysis were used as catalysts. Catalytic performance at high and low temperature was evaluated in order to investigate a broad range of temperature, which is one of the most critical condition in term of catalyst activity and deactivation, besides energy saving. The possible effect of impurities

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contained in less purified feedstocks is also discussed. Stable performance up to 100 h-on-stream was attained even under stressing reaction conditions.

*Keywords:* Bioethanol; Steam reforming; Second generation biofuels; Process intensification; Ni-based catalysts.

## **1 - INTRODUCTION**

Biofuels industry offers a large potential and real opportunity to solve the greenhouse gases (GHG) emission issue and the dependence from imported fossil fuels. Bio-ethanol, in particular, is the most common renewable fuel worldwide. Innovative and advanced routes for its valorisation are very interesting, *e.g.* conversion to ethylene [1], ethylene oxide (EO) and/or mono-ethylene glycol (MEG) [2]. Furthermore, consolidated industrial processes can be adapted to ethanol, to take advantage of mature and high efficiency processes. This idea is one of the pillars of the bio-refinery concept and represents the future of green industries [3]. The production of hydrogen starting from ethanol is considered a sustainable way to overcome its perspective increasing demand.

Today, 1<sup>st</sup> generation bio-ethanol is the most available commercially, used as fuel and gasoline additive, mainly produced in Brazil (from sugar cane) and USA (from corn). Nevertheless, 2<sup>nd</sup> generation bio-ethanol acquired increasing importance in the recent past [4] as a way to cope with ethical issues correlated with energy crops.

Scalable technologies for the transformation of lignocellulosic feedstock into fermentable sugars for the production of bioethanol or biochemicals are nowadays available. For instance, the Mossi Ghisolfi Group (M&G) developed a demonstrative plant for the fermentation of lignocellulosic materials in Crescentino, Italy, with a capacity of 40 kton/year of bioethanol. Generally, the biomass-to-ethanol technology is based on four main steps: pre-treatment, hydrolysis, fermentation and purification. The

first three steps were constantly improved by research and development of new enzymes and fermentation conditions [5]. The last step of purification remains critical because energy demanding [6], because the main sector for commercialization of bioethanol is the fuel market [7]. The purification line after the fermentation reactor is constituted mainly by distillation steps for the complete removal of impurities and water. Too high water content makes bioethanol unsuitable for blending with gasoline due to possible phase separation in the tank. Furthermore, a multistage separation based on vapor-liquid equilibria is required, due to the non ideal behaviour of the water/ethanol mixture, which leads to the formation of an azeotrope. The anhydrification stages consume up to 50-80% of the total energy required for the whole production process [6], therefore the possibility to use directly bio-ethanol without purification or with less expensive purification treatment looks very intriguing.

Steam Reforming is a consolidate technology able to convert hydrocarbons and water into hydrogen and carbon oxides. The reactions involved are favoured at high steam-to-carbon ratio due to the beneficial role of water in terms of coke gasification and hydrogen yield [7, 8]. As a consequence, Bio-Ethanol Steam Reforming (BESR) owns a huge potential. However, although mainly composed of water and ethanol, bio-ethanol typically contains other oxygenated and sulphur-containing compounds [7], which represent a not negligible issue for the process, especially using the common active phase for SR such as Ni [9]. The importance of impurities is not specifically addressed in most of the literature, since the scientific papers are mainly focused on ESR rather than BESR. For instance, Le Valant and co-workers studied the effect of various impurities, such as long-chain alcohols, amines, ethers and organic acids [10, 11]. They focused the attention on the main contaminants in 1<sup>st</sup> generation bio-ethanol obtained from sugar beet. The investigation was performed at high temperature (650°C). The work confirmed the key role of the contaminant concentrations.

This lack in the literature about the use of real crude bioethanol, especially the 2<sup>nd</sup> generation one, with the analysis of its contaminants with respect to sugar or starch derived ethanol [12], drove the

present work, starting with previous results obtained with pure ethanol [8, 13, 14]. The other major issue, is the economic feasibility of the process, which was recently studied by our group [15, 16]. These investigations clearly demonstrated that the use of diluted substrates is the key for the economic viability of the process.

Organic and inorganic impurities play an essential role in the deactivation phenomena on the catalyst [17]. At low temperature deactivation by coking becomes relevant and several organic impurities, possibly present in raw bioethanol, have been reported to enhance the rate of carbon formation. For instance long chain alcohols, which are the main impurities in bio-ethanol obtained by fermentation of sugar cane [11], can more easily dehydrate leading to unsaturated molecules. The latter show higher tendency to polymerize over the acid sites of the catalyst [18]. In addition, the adsorption of higher alcohols may compete with the adsorption of water and ethanol and affect the hydrophilic surface properties [19].

The presence of organo-sulphur compounds, such as dimethyl-sulphide or dimethyl-sulphoxide, is another possible source of catalyst deactivation. The amount of sulphur impurities in the broth formed after the fermentation stage depends on the biomass used and the operating conditions adopted in the biological transformation process [12, 20]. The poisoning role of sulphurs is well known for the industrial SR processes, especially when nickel is used as active phase. Indeed, the formation of bulk  $\text{Ni}_x\text{S}_y$  is critical [21]. For higher concentration of these contaminants, desulphurization of bioethanol is mandatory [20]. Some reports about sulphur deactivation at high temperature ( $700^\circ\text{C}$ ) during the SR of ethanol and phenol were published, revealing a strong deactivation of Ni-based catalysts using a stream containing tetrahydrothiophene [22].

On the other hand, inorganic anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) have limited chemical interaction with the active phase, at difference with sulphur-containing compounds. Nevertheless, their presence could lead to the physical coverage of the active phase due to salts precipitation upon vaporisation of the feed and they may adsorb on the oxidic catalyst surface. This issue is shared in general with other

impurities, including carbonates, for the partial hindering of the active sites [23]. Chloride ions have an additional role because they may increase surface acidity of catalysts depending on the support used [24].

In the present work the influence of bio-ethanol purity at high and low reaction temperature was studied considering proper catalyst formulations, such as Ni/La<sub>2</sub>O<sub>3</sub>, Ni/ZrO<sub>2</sub> and Ni/CaO-ZrO<sub>2</sub> [25, 26]. The use of differently purified 2<sup>nd</sup> generation bio-ethanol obtained mainly from Arundo Donax, a widely spread wild cane, growing on marginal lands, with minimum water input, integrated with wheat straw available locally, has never been explored up to now. The effect of substrate compositions in BESR was studied at different temperature. The study of bio-ethanol purity over a broad range of operating conditions helps also to understand its contribution to catalyst deactivation. A durability tests was also performed under the most critical operating conditions.

## **2 - Experimental**

### **2.1 Preparation of catalysts by flame pyrolysis**

A set of Ni-based catalysts was prepared by flame spray pyrolysis (FP) using a home-made apparatus, comprehensively described elsewhere [27, 28]. This method of synthesis allows the continuous preparation of nanopowdered oxides. Commercial scale apparatus is available on the market, which can lead to kg-scale production. The reproducibility is typically good since it is not a batch to batch process, but a continuous one. The details of the synthetic parameters adopted (precursor concentration, pressure drop across the nozzle, liquid flow rate) are deeply explained in other works [25, 26]. Briefly, samples were prepared diluting Zirconium acetyl-acetonate or lanthanum acetate, the alkaline precursor and Nickel (II) acetate tetrahydrate in a mixture 1:1 (vol/vol) of o-xylene and propionic acid. The proper concentration of the precursors solution was chosen in order to optimize the opposite effect of production rate (favoured by higher concentration of the precursors) and

aggregation phenomena (more likely with increasing particle density in the flame) [27]. The solution was fed to the burner using a 50 ml glass syringe with a flow rate of 2.2 ml/min and co-fed with 5 L/min of O<sub>2</sub>. The expected value of flame temperature, *ca.* 1500°C [29, 30], was ensured by the selected propionic acid / o-xylene ratio and the decomposition of acetate precursors, whose combustion contributes to increase the total combustion enthalpy, and by selecting proper pressure drop across the nozzle, liquid and oxygen flowrates. The reader is referred to specific publications on this technique to deepen the effect of preparation parameters on catalyst properties [27, 29–31]. In particular, pressure drop across the nozzle was set to 0.7 bar for the sample supported on La<sub>2</sub>O<sub>3</sub>, to be used for testing at high temperature (750°C), thus needing higher thermal resistance. 1.5 bar was used instead for the sample supported on ZrO<sub>2</sub>, to be tested at lower temperature, thus taking advantage of a higher surface area.

Ni loading was 10 wt% and CaO 9 wt%, as optimised in previous investigations [32, 33].

## **2.2 Activity testing for Bio-Ethanol Steam Reforming**

Activity tests were performed by means of a micropilot plant constituted by an Incoloy 800 continuous downflow reactor (i.d. 0.9 cm, length 40 cm), heated by an electric oven. The reactor temperature was controlled by an Eurotherm 3204 TIC.

The catalysts were pressed, ground and sieved into 0.15–0.25 mm particles and *ca.* 0.5 g were loaded into the reactor after dilution 1:3 (vol/vol) with SiC of the same particle size. Catalyst activation was accomplished by feeding 50 cm<sup>3</sup> min<sup>-1</sup> of a 20 vol% H<sub>2</sub>/N<sub>2</sub> gas mixture at 500 or 800°C for 1 h, depending on the testing temperature. During activity testing 0.017 cm<sup>3</sup> min<sup>-1</sup> of a 3:1 (mol/mol) water/ethanol liquid mixture were fed to the reactor by means of a Hitachi, mod. L7100, HPLC pump, added with 57 cm<sup>3</sup> min<sup>-1</sup> of N<sub>2</sub>, used as internal standard, and 174 cm<sup>3</sup> min<sup>-1</sup> of He. The liquid mixture was vaporised in the hot inlet of the reactor before reaching the catalyst bed. Such dilution of the feed

stream was calibrated so to keep the reactants mixture in the vapour phase even at zero conversion at the reactor outlet. The activity tests were carried out at atmospheric pressure, with a Gas Hourly Space Velocity (GHSV) of  $2,700 \text{ h}^{-1}$  (referred to the water/ethanol gaseous mixture). Analysis of outflowing gas was performed by a gas chromatograph (Agilent, mod. 7980) equipped with two columns connected in series (HPplot Q and Molecular Sieves) with a thermal conductivity detector (TCD), properly calibrated for the detection of ethanol, acetaldehyde, acetone, acetic acid, water, ethylene, CO, CO<sub>2</sub> and H<sub>2</sub>. Repeated analyses of the effluent gas were carried out every hour and the whole duration of every test at each temperature was 8 h. The raw data, expressed as mol/min of each species outflowing from the reactor, have been elaborated as detailed elsewhere [28, 34]. Material balance on C-containing products was used as first hand indicator to evaluate coke deposition.

The water/ethanol ratio was kept unchanged for all the tests in case adding the right amount of pure water to set the right proportion between the two reactants.

### **3 - Crude bio-ethanol production, purification and composition**

Two samples of crude bio-ethanol were kindly supplied by Biochemtex (<http://www.biochemtex.com/en>). In the fermentative reactor the biomass is mixed with enzymes and fermented, resulting in a broth with an ethanol concentration of approximately 8-10 vol% in the presence of residual carbohydrates. This broth is first roughly separated by a single stage distillation (flash) to obtain a bioethanol concentration *ca.* 50 wt%. Flash distillation is the simplest and cheapest method for the removing of these high boiling contaminants such as different sugars and higher alcohols [35]. Then, after continuous rectification and dehydration, pure ethanol is produced and commercialized for the fuel sector: a concentration stage to *ca.* 90 wt% bioethanol is followed by further anhydrication. The two different bio-ethanol solutions, *i.e.* 50 and 90 wt% were here tested as substrates for BESR, and labelled in the following as BE50 and BE90, respectively. The raw black broth before flash was not tested due to the suspended aggregates and high content of sugars.

Possible poisoning effects for the catalyst are of course correlated with the concentration and nature of the contaminants in the feed steam, therefore knowing the analytical compositions is a practical necessary requirement. In addition, lignocellulosic ethanol may contain higher concentration and variety of impurities compared to sugar- or starch-derived bioethanol (almost two times higher) [12].

The relevant data of composition of the two samples here considered are listed in Table 1. The composition reveals a common amount of oxygenated organic compounds combined with a progressive decrease of total acidity and conductivity (*i.e.* dissolved salts and ionic compounds) passing from BE50 to BE90. A detailed discrimination of the single compounds was not possible due to experimental limitations, anyway acidity in this kind of bio-ethanol is mainly due to acetic acid formed during the steam explosion step, in particular from the acetate groups present in the hemicellulosic fraction [35, 36]. Oxygenated compounds are mainly alcohols such as propanol, isobutanol and various acetates [24]. The high conductivity values confirmed the presence of salts, mainly nitrates and phosphates [12]. The samples were here used as such, without any filtration or further treatment.

**Table 1:** Analytical composition of differently purified 2<sup>nd</sup> generation bio-ethanol solutions (certificate of analysis from the quality control laboratory).

Parameters	Unit	BE90	BE50
<b>Ethanol + alcohol saturated content</b>	%(m/m)	89.7	50.2
<b>Other oxygenated compounds</b>	%(m/m)	-	0.15
<b>Mono-alcohol saturated (C3-C5)</b>	%(m/m)	0.37	-
<b>Methanol</b>	%(m/m)	0.27	0.1

<b>Water</b>	%(m/m)	9.66	49.6
<b>Total Acidity</b>	%(m/m)	0.0014	0.059
<b>Conductivity</b>	$\mu\text{S/m}$	159	2180
<b>Optic Appearance</b>	-	Clear and colourless	Opalescent
<b>Inorganic Chlorides</b>	mg/kg	0.14	0.1
<b>Copper</b>	mg/kg	0.02	0.02
<b>Phosphorous</b>	mg/l	0.02	0.02
<b>Non-volatile materials</b>	mg/100ml	1	5
<b>Sulphates</b>	mg/kg	0.86	1.0
<b>Sulphurs</b>	mg/kg	0.3	0.7

## 4. Results and Discussion

### 4.1 High Temperature activity tests

At first, high temperature reaction conditions (750 and 625°C) were explored. Generally these high operating temperatures (600-800°C) are chosen during the SR process in order to limit coke formation and to promote the complete conversion of possible byproducts (*e.g.* CH<sub>4</sub>) [7]. However, sintering may be relevant and deactivation phenomena due to the presence of sulphur impurities can be active in this temperature range. Generally, the sulphur issue is eliminated by the hydrodesulphurization of the inlet gas stream before the reformer, when relevant, whereas for sintering phenomena proper catalyst formulation has to be used. From this latter point of view, we have selected the present catalysts on the basis of preliminary testing with pure, anhydrous ethanol [37].

Testing at high temperature brought to full conversion, no C<sub>2</sub> byproducts and limited or even nil methane selectivity irrespectively of the ethanol or bioethanol feed (Table 2). Systematically, slightly worse performance was achieved when decreasing the purity of the feed. However, stable and

satisfactory performance was obtained at both 750 and 625°C, selecting this latter value as preferable temperature to decrease the heat input to the reformer in view of process intensification. Absence of methane production at 750°C using pure ethanol (AE) witnessed higher steam reforming activity without the impurities. The present results demonstrate the possibility to exploit diluted bioethanol solutions, characterised by much lower production cost, in spite of their lower purity. Indeed, no significant deactivation or dramatically worse catalytic performance was observed.

At 625°C negligible selectivity to acetaldehyde and ethylene and low methane yield were achieved. 100% carbon balance was obtained at 750°C and 625°C thanks to the negligible formation of carbon deposits coupled with very efficient C gasification by steam. Decreasing temperature led to a decrease of the CO/CO<sub>2</sub> ratio due to improvement of the WGS reaction. No significant change of these results was detected changing the bio-ethanol solution.

**Table 2:** Results of activity testing for BESR at high temperature using Ni/La<sub>2</sub>O<sub>3</sub>, 8 h-on-stream, data averaged out over 4-8 h-on-stream, GHSV = 2,700 h<sup>-1</sup>, Water/Ethanol = 3 (mol/mol). AE = Absolute Ethanol (99.9 vol%).

<i>Catalyst</i>	<i>Ni/La<sub>2</sub>O<sub>3</sub></i>								
	750			625			500		
<i>Temperature (°C)</i>	AE	Bio90	Bio50	AE	Bio90	Bio50	AE	Bio90	Bio50
<i>Ethanol purity</i>	AE	Bio90	Bio50	AE	Bio90	Bio50	AE	Bio90	Bio50
<i>H<sub>2</sub> productivity (mol min<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>)</i>	2.05 ± 0.03	1.29 ± 0.06	1.08 ± 0.08	1.97 ± 0.05	1.30 ± 0.04	1.18 ± 0.07	1.18 ± 0.05	1.23 ± 0.12	0.46 ± 0.01
<i>Sel. CH<sub>2</sub>CH<sub>2</sub> (%)</i>	0	0	0	0	0	0	0	0	0
<i>Sel. CH<sub>3</sub>CHO (%)</i>	0	0	0	0	0	0	0	0	11.4 ± 1.4
<i>Sel. CH<sub>4</sub> (%)</i>	0	2.8 ± 0.3	2.5 ± 1.2	2.2 ± 0.1	2.7 ± 0.3	2.8 ± 0.3	6.58 ± 0.04	12.6 ± 1.3	5.9 ± 0.6
<i>CO/CO<sub>2</sub></i>	2.60 ± 0.12	2.3 ± 0.3	2.7 ± 0.3	1.7 ± 0.1	1.7 ± 0.2	1.4 ± 0.2	0.68 ± 0.01	1.0 ± 0.3	0.53 ± 0.02

## 4.2 Low Temperature activity tests

Low temperature testing was added in order to compare catalytic activity under particularly stressing conditions. At 500°C or lower temperature, conspicuous energy saving can be achieved, however at the expenses of a generally lower H<sub>2</sub> productivity due to incomplete methane reforming [38]. Furthermore, coking is particularly relevant at this temperature due to inefficient coke steaming. Tests at 500°C with Ni/La<sub>2</sub>O<sub>3</sub> showed full ethanol conversion at the beginning of the test, but it decreased after 1 day-on-stream below 90%. Furthermore, some acetaldehyde started forming and a non-negligible amount of methane was present. Therefore, a catalyst formulation that revealed more active at lower temperature was used. Ni/ZrO<sub>2</sub> was chosen due to its high H<sub>2</sub> productivity and resistance toward coking [39].

Ni/ZrO<sub>2</sub> and Ni/CaO-ZrO<sub>2</sub> were activated and tested at 500°C. A deep characterization of the catalysts and preliminary activity testing with pure ethanol is reported elsewhere [33]. TPR characterization showed that this temperature was sufficient for the complete reduction of the whole amount of NiO for both catalysts [33].

The steam-to-ethanol ratio of the feed was maintained equal to 3 (stoichiometric molar ratio) for all the tests, in order to operate under critical conditions for carbon formation, without changing this key parameter, which directly affects H<sub>2</sub> yield and energy efficiency [7]. In particular, the higher the amount of water in the feed, the higher H<sub>2</sub> productivity because of the thermodynamic promotion of the WGS reaction and the gasification rate of coke [7]. By contrast, drawbacks are the lower thermal efficiency of the process due to the higher evaporation enthalpy of more diluted liquid mixtures [14]. However, the presence of excess water allows important heat recovery from the outlet stream, which may be used for feed preheating and evaporation [40–42].

Comparison between activity tests using pure ethanol (99.9 vol%) in the feed or BE90 is shown in Table 3 for the Ni/ZrO<sub>2</sub> sample. At 500°C a slight decrease of H<sub>2</sub> productivity and increase of methane selectivity was observed when using BE90 instead of absolute ethanol (99.9 vol%), which means that the small amount of impurities plays a marginal role. The CO/CO<sub>2</sub> ratio slightly increased, showing

a limited influence also on the WGS reaction. The same trend was obtained at 400°C. Traces of ethylene were sporadically detected when using BE90. Negligible ethanol conversion was attained at 300°C for all the solutions used, whereas full ethanol conversion was reached at 400 and 500°C irrespectively of the ethanol solution used.

However, in order to consolidate the possibility to operate at low temperature, coking resistance must be improved, *e.g.* by doping with basic promoters such as using Ni/CaO-ZrO<sub>2</sub>, which revealed the highest stability for prolonged catalytic runs [32]. The beneficial role of this basic promoter is in accordance with several reports in literature [43–45]. In general, tuning support formulation by using a proper basic promoter, allows to prevent ethanol dehydration and subsequent coking through ethylene polymerization. In addition, it enhances oxygen mobility, metal dispersion and water adsorption [32], with overall positive effect on activity and resistance to coking [26, 46].

Activity did not change appreciably when comparing BE90 and AE for catalyst Ni/CaO-ZrO<sub>2</sub> (Table 4): at 500°C and 400°C hydrogen productivity remained almost equal and only a small increase of methane selectivity was observed when using BE90. Full ethanol conversion was always obtained, whereas at 300°C ethanol conversion decreased, combined with a suppression of methane and hydrogen formation. At 300°C the main product was acetaldehyde, meaning insufficient activity of the catalyst for C-C bond cleavage at such a low temperature.

This catalyst revealed the best results, therefore BE50 was also tested. At 500°C and 400°C H<sub>2</sub> productivity was equal than that obtained with high purity feed and no decrease of catalytic activity was ever detected. The absence of acetaldehyde and the stable performance with time-on-stream suggested that no strong deactivation occurred due to the impurities contained in the feed. The slightly lower carbon balance can be attributed to higher carbon formation, due to the presence of longer chain alcohols. This point can be improved by tuning process conditions, such as increasing the water/ethanol ratio. The CO/CO<sub>2</sub> ratio remained constant or even lower during the test at 500°C, meaning that the impurities did not affect the WGS reaction.

A possible cause of deactivation can be the deposition of salts on the catalyst, considering the high conductivity of the BE50 sample. However, feed evaporation occurs in the initial hot part of the reactor, which is filled with inert quartz beads, excluding significant fouling of the catalyst. In the case of scale up, a guard bed should be provided to meet this point.

Another possible cause of failure is coking, particularly critical at low temperature (400-500°C) due to concomitant mechanisms for carbon formation and its insufficient gasification. The values of C-balance relative to the tests using Ni/CaO-ZrO<sub>2</sub> are summarized in Figure 1 at different temperature and are used as first hand indicator for coke deposition. The C-balance was comparable with that of the blank test (*i.e.* without catalyst) at every temperature. Slightly lower C balance was systematically achieved with BE50 with respect to purer feeds, indicating possibly higher coking rate over the sample. A decreasing catalyst performance with time-on-stream would be expected in the case of significant coking, but it was ruled out by observing a stable performance (Figure 2), at least in the short term [47]. It should be underlined that, in our previous experience, significant coking issues typically provoke fastly decreasing conversion and reactor blockage by fouling in the very first h-on-stream. Thus, stable performance up to 8 h-on-stream is a good indicator of very slow coking rate.

Volatile organic contaminants, in particular organic acids and higher alcohols are expected to be responsible of this slightly higher carbon formation in the case of BE50. In general coking phenomena are ascribed to three main routes: i) hydrocarbons decomposition; ii) Boudouard reaction; iii) olefins formation and polymerization [7]. However, at low temperature ( $\leq 500^\circ\text{C}$ ) the former route is unlikely from a thermodynamic point of view [48]. The oligomerization of olefins generated by substrate dehydration (ethylene in the case of ethanol), is a well known process, and occurs over the acidic sites of the support [32]. The presence of higher organic alcohols and oxygenated compounds increase the coke formation because of the easier dehydration and polymerization of the heavier alcohols, thus this route has been considered the predominant one. Therefore, by considering the stable behaviour with time-on-stream and the absence of C<sub>2</sub> byproducts (often appearing when Ni is progressively

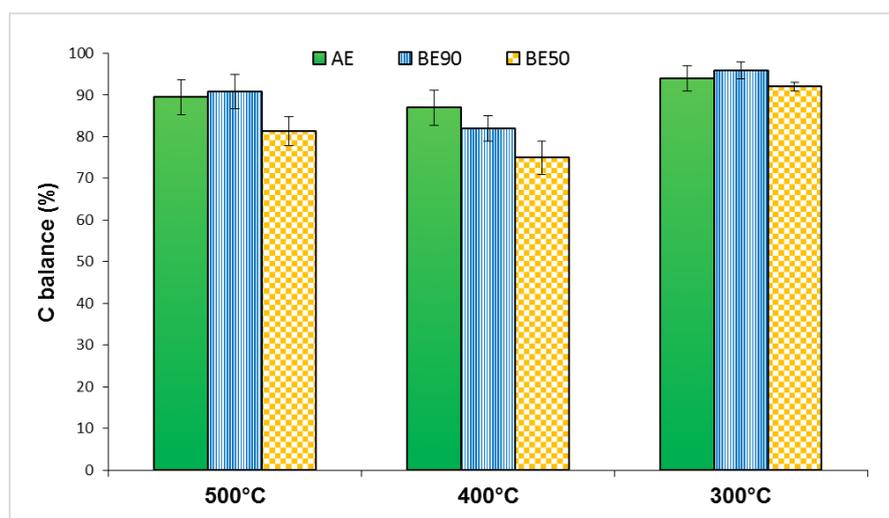
covered by encapsulating carbon) exclude significant Ni deactivation. Therefore, the slightly higher coking contribution observed with BE50 can be mainly ascribed to the residual acidic sites over the support surface.

**Table 3:** Results of activity testing for BESR at low temperature using Ni/ZrO<sub>2</sub>, 8 h-on-stream, Data Averaged out 4-8 h-on-stream, GHSV = 2,700 h<sup>-1</sup>, Water/Ethanol = 3 mol/mol. AE= absolute ethanol, 99.9 vol%.

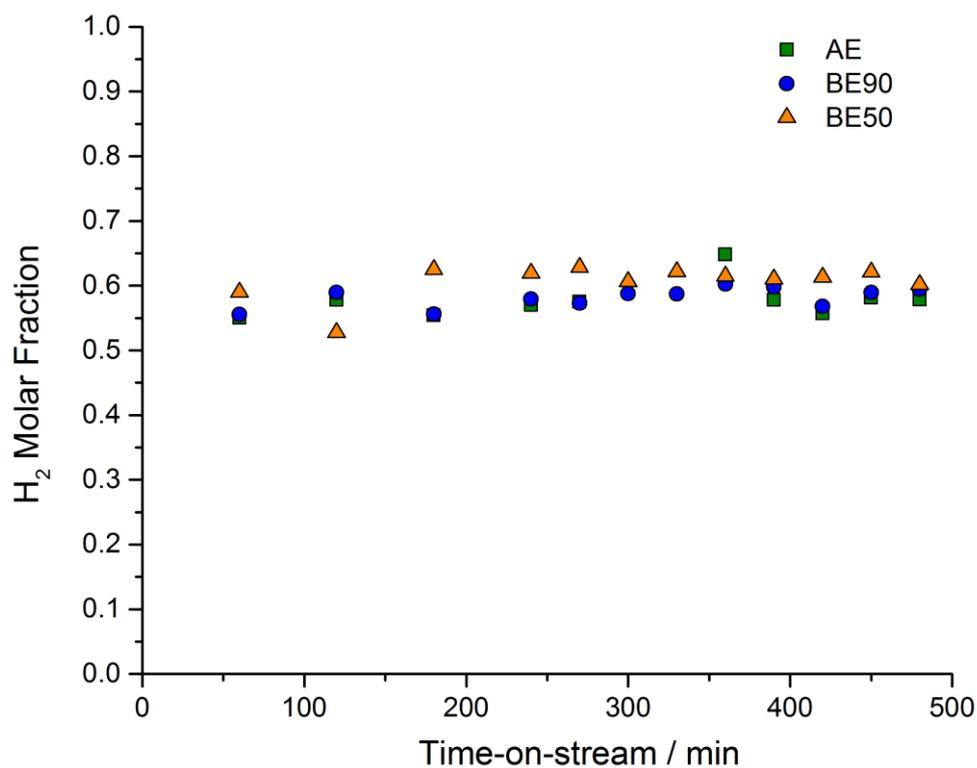
Catalyst	Ni/ZrO <sub>2</sub>			
	500		400	
Temperature (°C)				
Ethanol purity	AE	Bio90	AE	Bio90
H <sub>2</sub> productivity (mol min <sup>-1</sup> kg <sub>cat</sub> <sup>-1</sup> )	1.04±0.03	0.99±0.11	0.65±0.04	0.66±0.04
EtOH conversion (%)	100	100	100	100
Sel. CH <sub>2</sub> CH <sub>2</sub> (%)	0	2±2	0	0
Sel. CH <sub>3</sub> CHO (%)	0	0	0	0
Sel. CH <sub>4</sub> (%)	10.7±1.5	11.7±1.1	16±2	20±2
CO/CO <sub>2</sub>	0.82±0.14	0.9±0.2	1.2±0.2	1.29±0.07

**Table 4:** Results of activity testing for BESR at low temperature using Ni/CaO-ZrO<sub>2</sub>, 8 h-on-stream, Data Averaged out 4-8 h-on-stream, GHSV = 2,700 h<sup>-1</sup>, Water/Ethanol = 3 mol/mol. AE= absolute ethanol, 99.9 vol%.

Catalyst	Ni/CaO-ZrO <sub>2</sub>								
	500			400			300°C		
Temperature (°C)	AE	BE90	BE50	AE	BE90	BE50	AE	BE90	BE50
Ethanol purity	AE	BE90	BE50	AE	BE90	BE50	AE	BE90	BE50
H <sub>2</sub> productivity (mol min <sup>-1</sup> kg <sub>cat</sub> <sup>-1</sup> )	1.07±0.10	1.13±0.07	1.08±0.09	0.75±0.01	0.80±0.02	0.80±0.04	0	0	0
EtOH conversion (%)	100	100	100	100	100	100	34±4	29±3	22.5±1.4
Sel. CH <sub>2</sub> CH <sub>2</sub> (%)	0	0	0	0	0	0	0	0	0
Sel. CH <sub>3</sub> CHO (%)	0	0	0	0	0	0	76±5	73±1	83±6
Sel. CH <sub>4</sub> (%)	19±2	20±3	16±2	37±3	34±3	26±2	10±2	11.2±0.9	3±5
CO/CO <sub>2</sub>	0.64±0.10	0.65±0.10	0.52±0.10	0.20±0.02	0.24±0.04	0.42±0.04	/	/	/



**Figure 1:** Carbon balance for Ni/CaO-ZrO<sub>2</sub>, data averaged out on 4-8 h-on-stream, GHSV = 2,700 h<sup>-1</sup>, Water/Ethanol = 3 (mol/mol). Reference for C balance in a blank test (without catalyst) at 500°C: 91 ± 4.

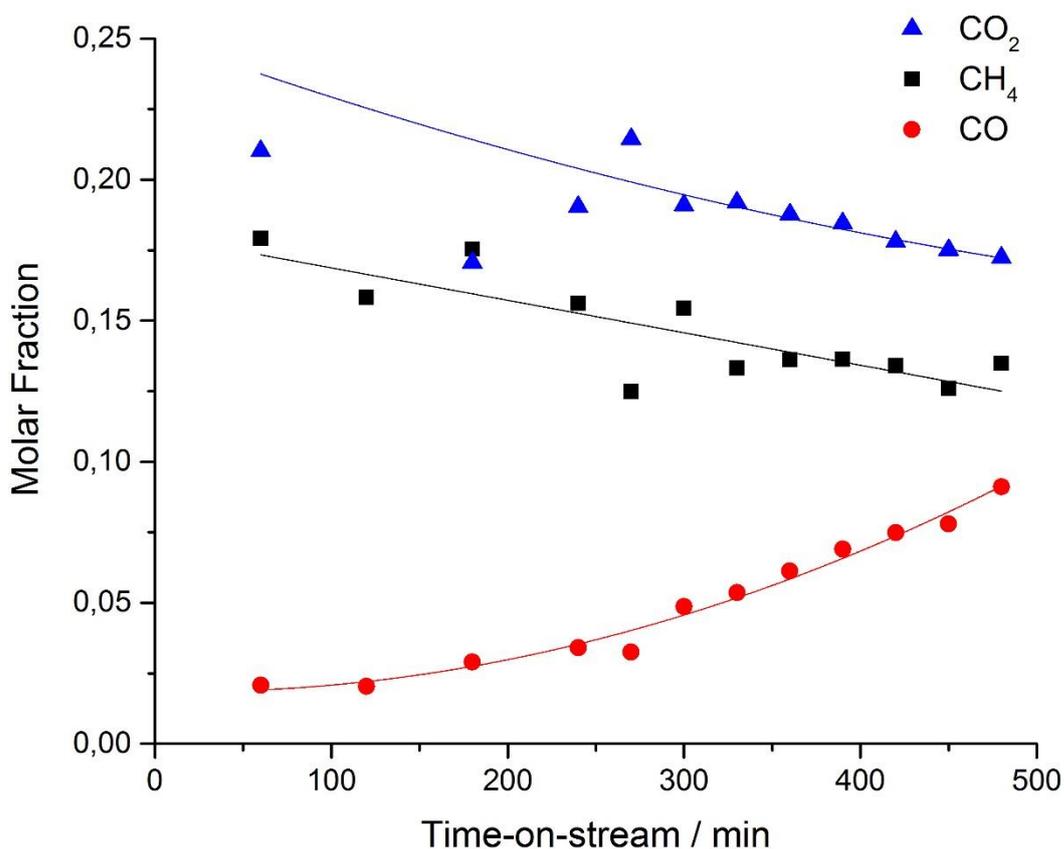


**Figure 2:** H<sub>2</sub> molar fraction at 400°C vs. time-on-stream for sample Ni/CaO-ZrO<sub>2</sub> with different feeds.

### 4.3 Low temperature activity testing: comparison of catalysts

The comparison between catalytic activity of Ni/ZrO<sub>2</sub> and Ni/CaO-ZrO<sub>2</sub> revealed a different behaviour toward the water gas shift reaction. This point is critical for Ni-based catalyst, which are less active toward this reaction with respect other metals like Fe, Cu and Co [19]. The decrease of temperature from 500°C to 400°C led to lower activity for this reaction for the undoped sample, as witnessed by the increase of CO/CO<sub>2</sub> ratio (Tables 3 and 4). The opposite behaviour was achieved for the CaO-doped sample. The same was obtained using both diluted bio-ethanol solutions, therefore a different mechanism characterised the two catalysts. The explanation of the lower performance of Ni/ZrO<sub>2</sub> for WGS was detailed in a previous work [33]. Using Ni/CaO-ZrO<sub>2</sub> the WGS reaction was enhanced decreasing the temperature to 400°C due to its exothermicity. However, a slight increase of the CO/CO<sub>2</sub> ratio was observed using feeds with decreasing purity (from 0.20 to 0.24 and 0.42, Table 4). This behaviour can be better explained on the basis of the time-on-stream trends in Figure 3, where a progressive increase of CO formation is combined with a decrease of CO<sub>2</sub> and CH<sub>4</sub> concentration. We can tentatively explain this behaviour considering that the higher concentration of higher alcohols when passing from AE to BE90 to BE50 can lead to slightly higher carbon deposition over support surface, especially at the lowest temperature, for which the coke gasification activity is more limited. This effect is not correlated to a decrease of catalytic activity of the Ni particles, which remain substantially unaltered. However, the support plays its own role by activating steam and supplying activated oxidising species to the C-based intermediates which are forming on the Ni particles. If the surface of the support changes its composition, support activity in activating water and surface mobility of activated oxydrils change, leading to unsteady products distribution with time-on-stream. Looking specifically to Figure 3, a further consideration can arise. The rate of disappearance of CH<sub>4</sub> and CO<sub>2</sub> is the same and corresponds to roughly half that of formation of CO. This can be correlated to a dry reforming reaction ( $\text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{CO} + 2 \text{H}_2$ ) occurring over the catalyst at low temperature. Likely, the reverse Boudouard reaction can also contribute to CO

formation at expenses of CO<sub>2</sub>. Thus, in general we may conclude that at low temperature CO<sub>2</sub> can partly act as oxidising agent, activated on the same Ni particle, if sufficient oxidising species are not transported through the support surface.

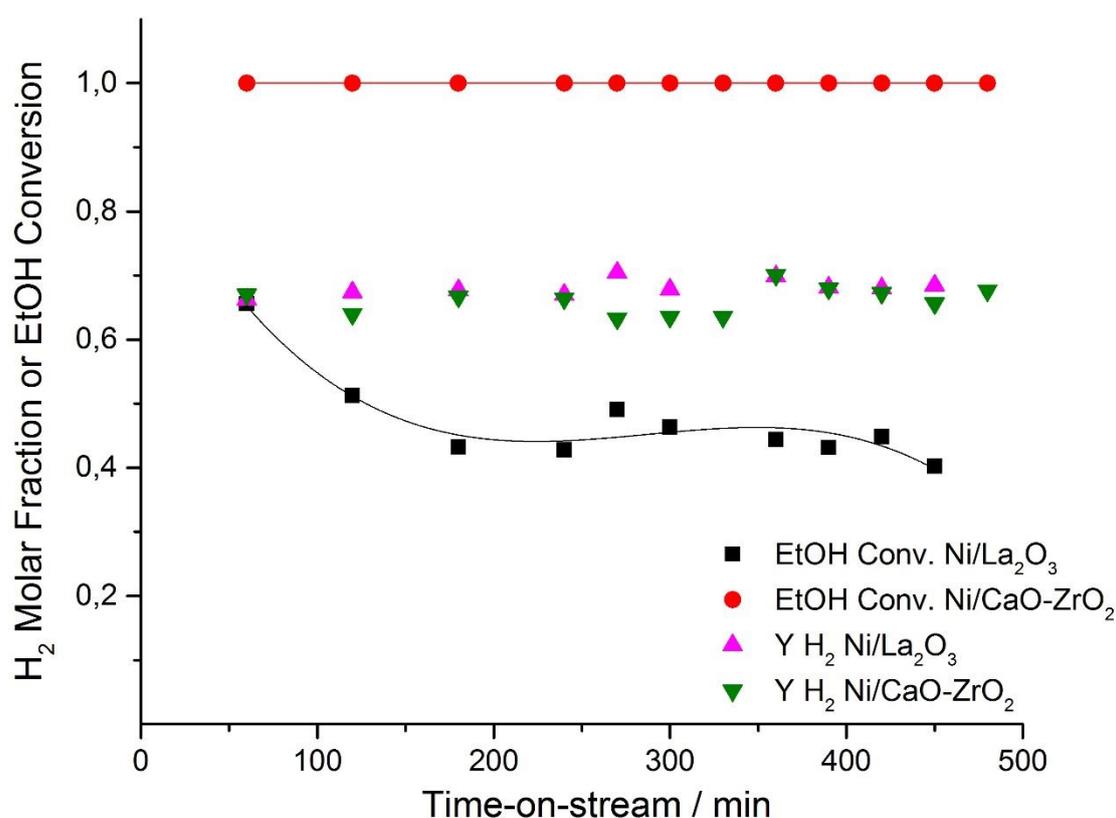


**Figure 3:** Product distribution vs. time-on-stream for BE50 tests using Ni/CaO-ZrO<sub>2</sub>, GHSV = 2,700 h<sup>-1</sup>, Steam/Ethanol = 3 mol/mol, T = 400°C.

#### 4.4 Comparison between different supports

A comparison between the two different support (La<sub>2</sub>O<sub>3</sub> and CaO-ZrO<sub>2</sub>) was carried out at 500°C. Results at 500°C using Ni/La<sub>2</sub>O<sub>3</sub> were largely unsatisfactory. Lantana was more suitable for higher operating temperature, as also reported in previous investigation [23]. Ni/CaO-ZrO<sub>2</sub> sample proved more effective at lower temperature (Figure 4), although some criticisms may arise due to coking

issues, which are instead not significant when using a basic support at high temperature. Doping with alkali and alkali-earth metal oxides can be a suitable way to improve the catalyst stability toward deactivation phenomena. Basic doping is an effective approach using traditional wet-methods, such as incipient wetness impregnation, co-precipitation and sol-gel methods [49–52], or Flame Spray Pyrolysis [53]. The calcium oxide doping of the  $ZrO_2$  is proven to limit the role of surface acidity on coking, especially at lower temperature as confirmed by our tests.



**Figure 4:** Comparison of H<sub>2</sub> molar fraction in the products distribution and ethanol conversion using BE50 for bio-ethanol SR tests over Ni/CaO-ZrO<sub>2</sub> and Ni/La<sub>2</sub>O<sub>3</sub> at 500°C.

#### 4.5 Durability tests

The catalyst performance has been tested up to 100 h-on-stream (5 days) at 500°C. The catalyst supported over lanthana confirmed insufficiently stable, showing decreasing conversion and increasing selectivity to acetaldehyde just after two days-on-stream when tested with BE90. By contrast, the zirconia supported catalyst was sufficiently stable with full ethanol conversion and stable carbon balance (comparable with the blank test) up to 5 days of continuous operation. A slight decrease of hydrogen productivity was observed when using BE90, corresponding to a corresponding increase of methane selectivity was observed. This allows to conclude that catalysts supported on ZrO<sub>2</sub> represent a substantially stable catalyst formulation, which suggests to proceed with process optimisation (e.g. fine tuning of temperature and water/ethanol ratio to cope with the slight decrease of productivity with time on stream. The stability for ZrO<sub>2</sub> supported samples was similar irrespectively of the presence of dopants and of the type of BE used.

**Table 5:** Durability tests over Ni/ZrO<sub>2</sub> and Ni/La<sub>2</sub>O<sub>3</sub> at 500°C for different days (DX).

	BE90					BE50	
	Ni/La <sub>2</sub> O <sub>3</sub>		Ni/ZrO <sub>2</sub>			Ni/ZrO <sub>2</sub>	
	D1	D2	D1	D2	D5	D1	D5
500°C							
CO/CO <sub>2</sub>	1.0 ± 0.3	-	0.73 ± 0.14	0.77 ± 0.15	0.72 ± 0.09	0.8 ± 0.2	0.7 ± 0.2
C balance (%)	90 ± 7	-	91 ± 2	92 ± 3	90 ± 4	91 ± 3	94 ± 4
Conv. EtOH	1	< 90	1	1	1	1	1
H <sub>2</sub> productivity (mol/min kg <sub>cat</sub> )	1.2 ± 0.1	0.72 ± 0.2	1.28 ± 0.03	1.19 ± 0.08	1.14 ± 0.08	1.22 ± 0.15	1.19 ± 0.10

S <sub>CH<sub>3</sub>CHO</sub> (%)	-	> 5	-	-	-	-	-
S <sub>CH<sub>4</sub></sub> (%)	11.7 ± 1.9	-	7.4 ± 1.1	8.2 ± 1.2	10 ± 3	11.6 ± 1.4	9.8 ± 0.5
S <sub>C<sub>2</sub>H<sub>2</sub></sub> (%)	-	-	-	-	-	-	-

## Conclusion

The exploitation of crude or partially purified bio-ethanol allows to build a stronger basis for the industrial application of steam reforming. In this work the investigation of real 2<sup>nd</sup> generation bioethanol was carried out considering different purification strategies. Organic and inorganic impurities in raw bio-ethanol can cause serious deactivation of the steam reforming catalyst. Ni/La<sub>2</sub>O<sub>3</sub> was selected as catalyst for high temperature testing (625-750°C), where it proved very stable and selective. Low temperature tests (300-500°C) were also carried out, aiming at overall process intensification. In this temperature range, coking is the main concern as for stability, which may be affected, besides by the catalyst formulation, by the impurities contained in less purified feeds. For instance, alcohols with longer chain than ethanol, sulphur and salts can significantly deactivate the catalyst.

Fouling by salts can be prevented by using an inert solid guard bed during vaporisation of the feed. No significant loss of catalytic activity for Ni/ZrO<sub>2</sub> and Ni/CaO-ZrO<sub>2</sub> catalysts was observed, although a slight increase of carbon formation occurred. Better results at lower temperature were achieved with the zirconia supported samples with respect the Ni/La<sub>2</sub>O<sub>3</sub> one. Durability tests confirmed a substantial stability of the ZrO<sub>2</sub>-based catalysts, when operated at 500°C, with slight change of products distribution and hydrogen productivity that may be further optimised by fine tuning of the process variables.

At last, we have already discussed the advantages in terms of process intensification of the use of diluted bioethanol solutions coupled with low temperature steam reforming. Indeed, this implies the use of a less expensive feed and lower heat input to the reformer. The present work demonstrates that the residual impurities contained in the less purified feed (down to 50 wt%) have limited effect on catalyst performance and stability, provided that the catalyst formulation is properly optimised. Thus, BE50 is a suitable feed for ethanol steam reforming.

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## References

1. Chen G, Li S, Jiao F, Yuan Q (2007) Catalytic dehydration of bioethanol to ethylene over TiO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts in microchannel reactors. *Catal Today* 125:111–119 . doi: 10.1016/j.cattod.2007.01.071
2. Posada JA, Patel AD, Roes A, et al (2013) Potential of bioethanol as a chemical building block for biorefineries: Preliminary sustainability assessment of 12 bioethanol-based products. *Bioresour Technol* 135:490–499 . doi: 10.1016/j.biortech.2012.09.058
3. Rass-Hansen J, Christensen CH, Sehested J, et al (2007) Renewable hydrogen: carbon formation on Ni and Ru catalysts during ethanol steam-reforming. *Green Chem* 9:1016 . doi: 10.1039/b702890c
4. Escobar JC, Lora ES, Venturini OJ, et al (2009) Biofuels: Environment, technology and food security. *Renew Sustain Energy Rev* 13:1275–1287 . doi: 10.1016/j.rser.2008.08.014
5. Alonso DM, Bond JQ, Dumesic JA (2010) Catalytic conversion of biomass to biofuels. *Green Chem* 12:1493–1513 . doi: 10.1039/c004654j
6. Lee F, Pahl RH (1985) Solvent Screening Study and Conceptual Extractive Distillation Process to Produce Anhydrous Ethanol from Fermentation Broth. *Ind Eng Chem Process Des Dev* 24:168–172
7. Mattos L V., Jacobs G, Davis BH, Noronha FB (2012) Production of hydrogen from ethanol: Review of reaction mechanism and catalyst deactivation. *Chem Rev* 112:4094–4123 . doi: 10.1021/cr2000114
8. Rossetti I, Compagnoni M, Torli M (2015) Process simulation and optimisation of H<sub>2</sub> production from ethanol steam reforming and its use in fuel cells. 1. Thermodynamic and kinetic analysis. *Chem Eng J* 281:1024–1035 . doi: 10.1016/j.cej.2015.08.025

9. Seelam PK, Liguori S, Iulianelli A, et al (2012) Hydrogen production from bio-ethanol steam reforming reaction in a Pd/PSS membrane reactor. *Catal Today* 193:42–48 . doi: 10.1016/j.cattod.2012.01.008
10. Le Valant A, Garron A, Bion N, et al (2011) Effect of higher alcohols on the performances of a 1%Rh/MgAl<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst for hydrogen production by crude bioethanol steam reforming. *Int J Hydrogen Energy* 36:311–318 . doi: 10.1016/j.ijhydene.2010.09.039
11. Le Valant A, Can F, Bion N, et al (2010) Hydrogen production from raw bioethanol steam reforming: Optimization of catalyst composition with improved stability against various impurities. *Int J Hydrogen Energy* 35:5015–5020 . doi: 10.1016/j.ijhydene.2009.09.008
12. Habe H, Shinbo T, Yamamoto T, et al (2013) Chemical Analysis of Impurities in Diverse Bioethanol Samples. *J Japan Pet Inst* 56:414–422
13. Rossetti I, Biffi C, Tantardini GF, et al (2012) 5 kW e + 5 kW t reformer-PEMFC energy generator from bioethanol first data on the fuel processor from a demonstrative project. *Int J Hydrogen Energy* 37:8499–8504 . doi: 10.1016/j.ijhydene.2012.02.095
14. Rossetti I, Compagnoni M, Torli M (2015) Process simulation and optimization of H<sub>2</sub> production from ethanol steam reforming and its use in fuel cells . 2 . Process analysis and optimization. *Chem Eng J* 281:1036–1044 . doi: 10.1016/j.cej.2015.08.045
15. Compagnoni M, Mostafavi E, Tripodi A, et al (2017) Techno-economic analysis of a bioethanol to hydrogen centralized plant. *Energy&Fuels* 31:12988–12996
16. Compagnoni M, Tripodi A, Mostafavi E, et al (2017) Hydrogen Production by Steam Reforming of Bio-ethanol : Process Design and Economic Assessment. *DGMK Tagungsbericht* 2017:5–11
17. Mondal T, Pant KK, Dalai AK (2015) Oxidative and non-oxidative steam reforming of crude bio-ethanol for hydrogen production over Rh promoted Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst. *Appl Catal A Gen* 499:19–31 . doi: 10.1016/j.apcata.2015.04.004
18. Trimm DL (1997) Coke formation and minimisation during steam reforming reactions. *Catal Today* 37:233–238 . doi: 10.1016/S0920-5861(97)00014-X
19. Hou T, Zhang S, Chen Y, et al (2015) Hydrogen production from ethanol reforming: Catalysts and reaction mechanism. *Renew Sustain Energy Rev* 44:132–148 . doi: 10.1016/j.rser.2014.12.023
20. Chaichanawong J, Yamamoto T, Ohmori T, Endo A (2010) Adsorptive desulfurization of bioethanol using activated carbon loaded with zinc oxide. *Chem Eng J* 165:218–224 . doi: 10.1016/j.cej.2010.09.020
21. Torres W, Pansare SS, Goodwin JG (2007) Hot Gas Removal of Tars, Ammonia, and Hydrogen Sulfide from Biomass Gasification Gas. *Catal Rev* 49:407–456 . doi: 10.1080/01614940701375134
22. Garbarino G, Lagazzo A, Riani P, Busca G (2013) Steam reforming of ethanol-phenol mixture on Ni/Al<sub>2</sub>O<sub>3</sub>: Effect of Ni loading and sulphur deactivation. *Appl Catal B Environ* 129:460–472 . doi: 10.1016/j.apcatb.2012.09.036
23. Forzatti P (1999) Catalyst deactivation. *Catal Today* 52:165–181 . doi: 10.1016/S0920-5861(99)00074-7
24. Bion N, Duprez D, Epron F (2012) Design of nanocatalysts for green hydrogen production from bioethanol. *ChemSusChem* 5:76–84 . doi: 10.1002/cssc.201100400
25. Compagnoni M, Lasso J, Di Michele A, Rossetti I (2016) Flame-pyrolysis-prepared catalysts for the

steam reforming of ethanol. *Catal Sci Technol* 6:6257 . doi: 10.1039/c5cy01958c

26. Compagnoni M, Tripodi A, Di Michele A, et al (2017) Low temperature ethanol steam reforming for process intensification: New Ni/MxO-ZrO<sub>2</sub> active and stable catalysts prepared by flame spray pyrolysis. *Int J Hydrogen Energy* 42:28193–28213 . doi: 10.1016/j.ijhydene.2017.09.123
27. Chiarello GL, Rossetti I, Forni L (2005) Flame-spray pyrolysis preparation of perovskites for methane catalytic combustion. *J Catal* 236:251–261
28. Rossetti I, Biffi C, Bianchi CL, et al (2012) Ni/SiO<sub>2</sub> and Ni/ZrO<sub>2</sub> catalysts for the steam reforming of ethanol. *Appl Catal B Environ* 117–118:384–396 . doi: 10.1016/j.apcatb.2012.02.006
29. Chiarello GL, Rossetti I, Lopinto P, et al (2006) Preparation by flame spray pyrolysis of ABO<sub>3</sub> catalysts for the flameless combustion of methane. *Catal Today* 117:549–553 . doi: 10.1016/j.cattod.2006.06.018
30. Chiarello GL, Rossetti I, Forni L, et al (2007) Solvent nature effect in preparation of perovskites by flame pyrolysis. 2. Alcohols and alcohols + propionic acid mixtures. *Appl Catal B Environ* 72:227–232 . doi: 10.1016/j.apcatb.2006.10.026
31. Chiarello GL, Rossetti I, Forni L, et al (2007) Solvent nature effect in preparation of perovskites by flame-pyrolysis. 1. Carboxylic acids. *Appl Catal B Environ* 72:218–226 . doi: 10.1016/j.apcatb.2006.11.001
32. Nichele V, Signoretto M, Pinna F, et al (2014) Ni/ZrO<sub>2</sub> catalysts in ethanol steam reforming: Inhibition of coke formation by CaO-doping. *Appl Catal B Environ* 150–151:12–20 . doi: 10.1016/j.apcatb.2013.11.037
33. Compagnoni M, Tripodi A, Di Michele A, et al Low Temperature Ethanol Steam Reforming: new Ni/MxO-ZrO<sub>2</sub> active and stable catalysts prepared by Flame Spray Pyrolysis. *Int J Hydrogen Energy* in press: . doi: 10.1016/j.ijhydene.2017.09.123
34. Ramis G, Rossetti I, Finocchio E, et al (2015) Metal Dispersion and Interaction with the Supports in the Coke Production over Ethanol Steam Reforming Catalysts. In: *Progress in clean energy*. pp 695–711
35. Rass-Hansen J, Johansson R, Møller M, Christensen CH (2008) Steam reforming of technical bioethanol for hydrogen production. *Int J Hydrogen Energy* 33:4547–4554 . doi: 10.1016/j.ijhydene.2008.06.020
36. Alvira P, Tomàs-Pejò E, Ballesteros M, Negro MJ (2010) Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresour Technol* 101:4851–4861 . doi: 10.1016/j.biortech.2009.11.093
37. Compagnoni M, Lasso J, Di Michele A, Rossetti I (2016) Flame pyrolysis prepared catalysts for the steam reforming of ethanol. *Catal Sci Technol* in press . doi: 10.1039/C5CY01958C
38. Mas V, Kipreos R, Amadeo N, Laborde M (2006) Thermodynamic analysis of ethanol/water system with the stoichiometric method. *Int J Hydrogen Energy* 31:21–28 . doi: 10.1016/j.ijhydene.2005.04.004
39. Rossetti I, Lasso J, Nichele V, et al (2014) Silica and zirconia supported catalysts for the low-temperature ethanol steam reforming. *Appl Catal B Environ* 150–151:257–267 . doi: 10.1016/j.apcatb.2013.12.012
40. Tripodi A, Compagnoni M, Martinazzo R, et al (2017) Process simulation for the design and scale up of heterogeneous catalytic process: Kinetic modelling issues. *Catalysts* 7: . doi:

10.3390/catal7050159

41. Rossetti I, Compagnoni M, Torli M (2015) Process simulation and optimization of H<sub>2</sub> production from ethanol steam reforming and its use in fuel cells. 2. Process analysis and optimization. *Chem Eng J* 281:1036–1044 . doi: 10.1016/j.cej.2015.08.045
42. Compagnoni M, Mostafavi E, Tripodi A, et al (2017) Techno-economic analysis of a bioethanol to hydrogen centralized plant. *Energy&Fuels* 31:12988–12996 . doi: 10.1021/acs.energyfuels.7b02434
43. Bachiller-Baeza B, Mateos-Pedrero C, Soria M a., et al (2013) Transient studies of low-temperature dry reforming of methane over Ni-CaO/ZrO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub>. *Appl Catal B Environ* 129:450–459 . doi: 10.1016/j.apcatb.2012.09.052
44. Xu L, Miao Z, Song H, et al (2014) Significant roles of mesostructure and basic modifier for ordered mesoporous Ni/CaO–Al<sub>2</sub>O<sub>3</sub> catalyst towards CO<sub>2</sub> reforming of CH<sub>4</sub>. *Catal Sci Technol* 4:1759 . doi: 10.1039/c3cy01037f
45. Lertwittayanon K, Atong D, Aungkavattana P, et al (2010) Effect of CaO-ZrO<sub>2</sub> addition to Ni supported on gamma-Al<sub>2</sub>O<sub>3</sub> by sequential impregnation in steam methane reforming. *Int J Hydrogen Energy* 35:12277–12285 . doi: 10.1016/j.ijhydene.2010.08.098
46. Nichele V, Signoretto M, Pinna F, et al (2014) Ni/ZrO<sub>2</sub> catalysts in ethanol steam reforming: Inhibition of coke formation by CaO-doping. *Appl Catal B Environ* 150–151:12–20 . doi: 10.1016/j.apcatb.2013.11.037
47. Garbarino G, Romero Perez A, Finocchio E, Busca G (2013) A study of the deactivation of low loading Ni/Al<sub>2</sub>O<sub>3</sub> steam reforming catalyst by tetrahydrothiophene. *Catal Commun* 38:67–73 . doi: 10.1016/j.catcom.2013.04.007
48. Navarro RM, Peña M a., Fierro JLG (2007) Hydrogen production reactions from carbon feedstocks: Fossil fuels and biomass. *Chem Rev* 107:3952–3991 . doi: 10.1021/cr0501994
49. Kusche M, Enzenberger F, Bajus S, et al (2013) Enhanced activity and selectivity in catalytic methanol steam reforming by basic alkali metal salt coatings. *Angew Chemie - Int Ed* 52:5028–5032 . doi: 10.1002/anie.201209758
50. Harshini, Lee DH, Jeong J, et al (2014) Enhanced oxygen storage capacity of Ce<sub>0.65</sub>Hf<sub>0.25</sub>M<sub>0.10</sub>O<sub>2-delta</sub> (M=rare earth elements): Applications to methane steam reforming with high coking resistance. *Appl Catal B Environ* 148–149:415–423 . doi: 10.1016/j.apcatb.2013.11.022
51. Pino L, Vita A, Cipitì F, et al (2011) Hydrogen production by methane tri-reforming process over Ni-ceria catalysts: Effect of La-doping. *Appl Catal B Environ* 104:64–73 . doi: 10.1016/j.apcatb.2011.02.027
52. Sanchez-Sanchez M., Navarro RM, Fierro JL. (2007) Ethanol steam reforming over Ni/M<sub>x</sub>O<sub>y</sub>Ni/M<sub>x</sub>O<sub>y</sub>–Al<sub>2</sub>O<sub>3</sub>Al<sub>2</sub>O<sub>3</sub> (M=Ce, La, Zr and Mg) catalysts: Influence of support on the hydrogen production. *Int J Hydrogen Energy* 32:1462–1471 . doi: 10.1016/j.ijhydene.2006.10.025
53. Pongthawornsakun B, Mekasuwandumrong O, Prakash S, et al (2015) Effect of reduction temperature on the characteristics and catalytic properties of TiO<sub>2</sub> supported AuPd alloy particles prepared by one-step flame spray pyrolysis in the selective hydrogenation of 1-heptyne. *Appl Catal A Gen* 506:278–287 . doi: 10.1016/j.apcata.2015.09.012