

Syngas production by catalytic steam gasification of citrus residues

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A B S T R A C T

This study investigate the feasibility to use citrus peel residues to produce hydrogen rich syngas by steam gasification process. Thermodynamic evaluations were performed by simulation modelling thus preliminary experiment was carried out at 1023 K and S/B ratio 1.5 wt/wt. The effect of different types of catalytic materials (minerals and synthetic catalyst) on steam gasification process was investigated in terms of efficiency, hydrogen formation tendency and outlet stream composition.

It is found that concentrations of H₂ and CO of 58.80 mol% and 25.34 mol% can be produced by citrus peels conversion. Moreover, both carbon and hydrogen gasification efficiencies can be enhanced using dolomite, MgO and Ni/Al₂O₃ in the reactor (from 43.7% to 54.9% and from 34.3% to 54.1% for CGE and H₂GE, respectively). Dolomite resulted the best catalyst for citrus peels steam gasification under the examined operative condition with CGE and H₂GE rates of 54.9% and 54.1%, respectively. Ni catalyst resulted to be affected by carbon formation and sintering on time on stream.

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Introduction

Due to increasing concern about environmental issues such as global warming and depletion of fossil fuels, hydrogen is considered an important energetic vector of the future. In fact, hydrogen can provide for energy in transportation and distributed heat and power generation with no effect on the environment, mainly when it is applied to fuel cells systems [1–5]. However, how to store hydrogen easily and cheaply is still a big problem. In fact, till now, none of the materials and methods for hydrogen storage has been found to meet all requirements for commercial electric vehicle applications [6,7]. Today hydrogen is generated mostly from fossil fuels with a

consequent, release of CO₂ during its production stage, while the use of biomass, as hydrogen tank, represent an attractive alternative to use a renewable source of energy. Hence, studies on biomass thermochemical conversion processes coupled with different reactor configurations have been carried out to serve different purposes, such as developing of fuels processor units [8–10], measuring in the thermography field [11–13], production of biofuels [14–16].

Among biomass typologies agro-industrial residues are obtained in large quantities as a result of industrial processing of fruits and vegetables [17]. The mainly production of citrus fruits juice in Italy is based on oranges and lemons with an annual consume of about 3.8 million tons (Sicily is the main

Italian fruits producer region with about 87% of the national share). Therefore, every year in Italy, the juice industries produce about 1 million tons of peel waste that represent an environmental problem related to disposal of solid wastes [18]. The conversion of waste materials or industrial byproducts into useful energy can be achieved through thermochemical and biochemical processes [19,20]. Ahmed and Gupta [21], evaluated the performances of both pyrolysis and gasification processes applied to food waste in terms of syngas flow rate, hydrogen flow rate, output power, total syngas yield, total hydrogen yield, total energy yield, and apparent thermal efficiency. They found that gasification was more favorable process for this kind of biomass than pyrolysis, but was noticed that longer time has needed to finish the gasification process. Results also demonstrate that food waste offers a good potential for solid waste thermal treatment with the specific aim of power generation. On the other side, the treatment of orange peels through biological processes resulted inhibited by presence of limonene, which constitutes about 95% of the orange peels oil [22]. Others reported that the bio-oil coming from pyrolysis of citrus wastes has been produced with higher yields than other biomass waste [23,24]. Nevertheless, L. Aguiar et al. [25], revealed that the citrus peel pyrolysis oil can be produced but with low quality due to the high oxygen content, thus it needs a catalytic upgrading prior that it can be used as a fuel or chemical.

On the whole, the specific properties of the processed waste/byproduct/residues significantly affect the conversion performances of thermochemical processes. In particular, some chemical-physical characteristics (i.e. elemental composition, lower heating value, ash content, moisture content, volatile matter content, bulk density, size and contaminants: N, S, Cl, heavy metals, etc.), are so decisive that pre-treatments of the feedstock are often applied before most of prevailing gasification technologies [26,27]. However, gasification has some advantages related to possibility of coupling the operating conditions (in particular, temperature and equivalence ratio) and the features of the specific reactor (fixed bed, fluidized bed, moving grate furnace, plasma reactor) to obtain a syngas suitable for different applications. Furthermore, the gasification process, when conducted using steam as gasifying agent can increase the outlet gas stream in terms of both heating value and hydrogen content [17,26]. The use of catalysts could play a crucial role in increasing the gasification efficiency. In fact, the catalysts promote tar conversion into combustible gas via thermal cracking, hydro-cracking or water gas shift reactions [28,29]. In this context, dolomite and other mineral materials as catalysts has attracted much attention because of their low cost and also can significantly reduce the tars content [30]. At the same time, the Ni-based catalysts are commercially available and they are extensively used for biomass gasification due also to their known activity in naphtha and methane reforming reactions [30].

Although, many papers are present in literature on food waste conversion through thermochemical processes, to the best of our knowledge, there are no works available on the behavior of citrus peel residues working under catalytic steam gasification. Indeed, to date, it is possible to find a research work of the authors developing a non-catalytic air-steam gasification campaign of citrus peel in a fluidized bed reactor [31].

Furthermore, Gadek et al. carried out comparative experiments of air gasification of different biomasses, including citrus peel, in a batch reactor [32]. Accordingly, the aim of this work was to investigate the feasibility to use this type of biomass feedstock to produce hydrogen rich syngas. Preliminary thermodynamic evaluations on citrus peels steam gasification were performed by a simulation modelling; therefore the comparison with experimental data was carried out through a blank no-catalyst test. Successively, attentions were addressed on the effect of different catalytic materials (minerals and synthetic catalyst) on steam gasification process in terms of efficiency, hydrogen formation tendency and outlet stream composition.

Experimental

Raw material treatment and characterization

The citrus peels were preventively air dried (383 K for 1 h), shredded and sieved into a grain size range of 25–40 mesh.

Proximate analysis included measurement of moisture, volatile matter, fixed carbon and ash content. The moisture measurement were performed on biomass samples, dried in a convection oven at 383 K until constant weight was recorded. The volatile matter content was determined by measuring weight loss after heating biomass samples to 1223 ± 20 K in an alumina crucible under N_2 atmosphere (ASTM D-2013). The ash content was measured by heating samples (Standard E-1755-01) at 848 ± 25 K for 3 h to constant weight in a muffle furnace and the fixed carbon fraction was calculated by subtracting the percentages of volatile matter, moisture and ash content. Elemental analysis was performed on both biomass samples and bio-char using Thermo Fisher Scientific (Flash EA 1112) CHNS-O Elemental Analyzer. Ultimate and proximate analysis data were reported in Table 1.

Based on the elemental composition and according to literature [14,33,34], High Heating Values (HHV) and Lower Heating Value (LHV) of biomass, were calculated with following equations:

$$\text{HHV(OLS)} = 1.87(\text{C})^2 - 144(\text{C}) - 2802(\text{H}) + 63.8(\text{C}*\text{H}) + 129(\text{N}) + 20147 \quad (1)$$

$$\text{HHV(PLS)} = 5.22(\text{C})^2 - 319(\text{C}) - 1647(\text{H}) + 38.6(\text{C}*\text{H}) + 133(\text{N}) + 21028 \quad (2)$$

Table 1 – Properties of citrus peels.

Ultimate Analysis (%)						
	C	H	N	S	O ^a	Ash
As received	34.1	5.0	1.0	0.1	32.6	6.9
Dry Basis	42.9	6.3	1.3	0.1	40.8	8.5
Proximate Analysis (%)					HHV	LHV
Moisture	VM	FC	Ash	(MJ/kg)	(MJ/kg)	
20.0	57.5	15.5	6.9	14.41	13.84	

^a By difference.

$$LHV = HHV - h_g(9H/100 - M/100) \quad (3)$$

HHV of biomass sample was calculated with an average of ordinary least-squares regression (OLS, eq. (1)) and a partial least-squares regression (PLS, eq. (2)) methods. Differently LHV was calculated with eq. (3), where H, M and h_g are hydrogen percentage, moisture percentage and latent heat of steam, respectively, on as received basis.

Thermogravimetric analysis

Thermo-decomposition of citrus peels was investigated by thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) measurements under nitrogen and steam atmosphere using a NETZSCH STA 449 F3 Jupiter TG analyzer. TGA/DTG analysis has been permitted to investigate on thermal behavior of the citrus residues depending on temperature and oxidant agent. Analysis were conducted in a temperature range from 298 K to 1173 K with a heating rate of 10 K min^{-1} and nitrogen atmosphere condition; while under steam atmosphere the temperature range analyzed was: 373 K–1173 K, and this is due to evaporating of the water.

Gasification measurements

Experiments were carried out at 1023 K and atmospheric pressure in a fixed bed stainless steel reactor ($h = 600 \text{ mm}$; i.d. = 12 mm) equipped with a mobile furnace, Fig. 1. About 2 g of citrus peels (grain size = 0.7–0.4 mm) were packed in the reactor and a flow of nitrogen was fed to the reactor. The furnace was heated to the analysis temperature and then was moved toward the biomass-bed. Successively, steam was purged inside the reactor with a steam on biomass ratio (S/B) of 1.5 wt/wt. The $\text{H}_2\text{O}_{(l)}$ flow was fed by an isocratic HP 1100 pump and vaporized in a stainless steel reactor held at 503 K. All tests were run for 2 h.

The total outlet gas stream was cooled at - 351 K by three traps through liquid nitrogen and ethyl acetate mixture, thus two separate phases (syngas and tar) were obtained.

The syngas volume was quantitatively measured by Agilent gas flow-meter ADM 2000, while a qualitative analysis in terms of “dry” syngas composition was determined by on line GC system (Agilent HP 6890 Plus) equipped with TCD/FID detectors. While the amount of tars produced was weighed by Mettler AE 166 analytical balance.

Catalytic measurements were performed by addition of 400 g (16–25 mesh) of catalyst (Dolomite, MgO and Ni/CaO- Al_2O_3) to the biomass packed bed.

Ni/CaO- Al_2O_3 is a commercial catalyst nominally made by 15 wt% of Ni supported on $\alpha\text{-Al}_2\text{O}_3$ (73 wt%) and CaO (8 wt%) mixture; it was activated before each gasification test (ex situ) at 1023 K under about 100 cc/min of hydrogen flow per 1 h.

Carbon gasification efficiency (CGE) and hydrogen gasification efficiency (HGE) were calculated following the equations below reported [35,36]:

$$\text{CGE}(\%) = \left(\frac{C_s \cdot F_s}{C_b \cdot F_b} \right) \cdot 100 \quad (4)$$

$$\text{H}_2\text{GE} = \frac{H_p \cdot 100\%}{H_r} \quad (5)$$

Where, C_s is the carbon content in the syngas, F_s is the syngas flow rate, C_b is the carbon content in the fed biomass, F_b is the biomass load, H_p is the mass of hydrogen in gaseous products and H_r is the mass of hydrogen in reactants (biomass + SR water).

Results and discussions

Citrus peels thermal behavior

The thermo-gravimetric analysis carried out on citrus peels samples under nitrogen and water atmosphere is reported in Fig. 2.

Under inert condition the TG analysis shows the citrus peels structure degradation in function of the temperature highlighting the main characteristics of this waste material. In

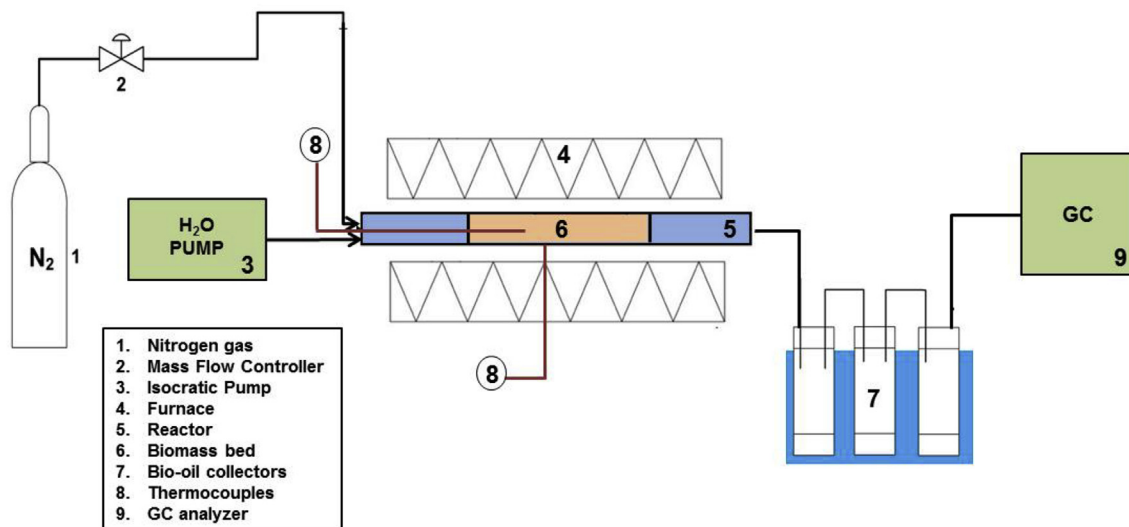


Fig. 1 – Scheme of lab-scale fixed bed gasification plant.

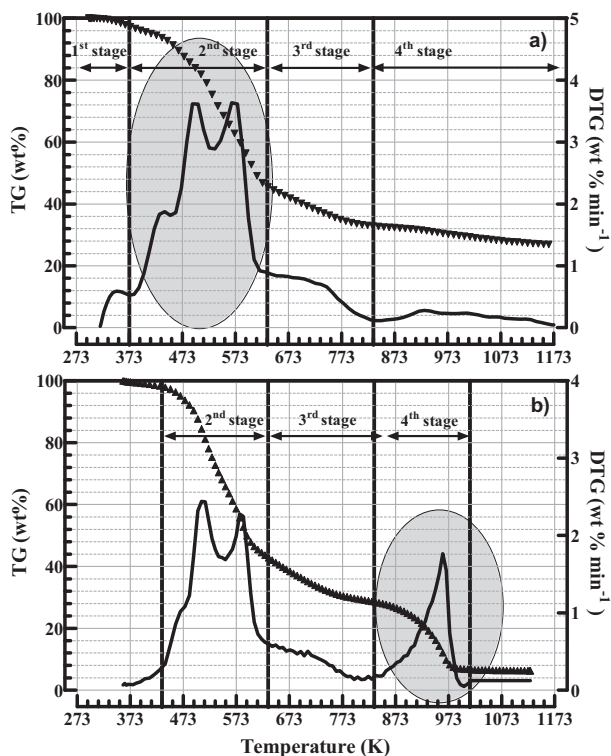


Fig. 2 – Thermo-gravimetric analysis of citrus peels in nitrogen (a) and steam (b) atmosphere.

particular, four stages can be distinguished during the sample heating process. The first stage, from room temperature to 373 K, represents the loss of the moisture. The second stage covers a broad range of temperature, from 373 K to 633 K, corresponding to hemicellulose and cellulose thermal activation present in the structure of the citrus peel (453 K and 503 K, respectively), followed by the scission and depolymerization reactions (peak at 573 K) with the formation of the volatiles products in according to the mechanism proposed in literature [37].

The third stage, from 633 K to 833 K, is related to the carbonaceous matter and solid residual. In detail, at 713 K (DTG curve) is highlighted a shoulder starting from 633 K, which is attributed to the presence of the lignin in the biomass sample.

Finally, in the last stage a slight continued loss of weight was registered until the end that correspond at the stabilization of the formed char that is related to the final residual matter in nitrogen atmosphere. The thermo-gravimetric test conducted in steam condition present the same TG curve and DTG peak obtained in nitrogen condition until 833 K except for the lack of the moisture before 373 K, due to the different starting temperature. In the third stage from 873 to 1013 K the steam presence provides to gasify the formed char with a further loss of weight which corresponds in the DTG curve at the peak formation at 953 K. The remained residue consist mainly in ashes, the mineral matter of the biomass. In Table 2 are reported the mainly DTG peaks related to the thermo-gravimetric tests. In particular, it is important to note that the TG citrus peels peaks related to the main thermal

Table 2 – Main peaks of citrus peels thermal decomposition.

Atmosphere	Temperature peaks (K)					
	I	II	III	IV	V	VI
Nitrogen	363	453	503	573	683	–
Steam	–	458	513	583	693	953

degradation (453 K and 573 K, nitrogen condition) result to be shifted to lower temperature than the TG peak recorded for white pine (643 K) [14], this suggests an easier thermal degradation of the citrus peels than woody biomass.

Experimental findings

Citrus peel residues were gasified with steam at 1023 K and $S/B = 1.5$ wt/wt, using different catalysts for a comparative evaluations in terms of gasification efficiencies and syngas compositions.

Firstly, thermodynamic evaluation of citrus peels steam gasification process was carried out in order to choice the appropriate operative condition in terms of S/B ratio. In particular, the steam gasification process was modelled by the authors through Aspen plus software, minimizing the Gibbs free energy, as described elsewhere [38]. Hence, thermodynamic equilibrium compositions containing permanent gaseous species (CO , CO_2 , H_2 and CH_4) at 1023 K were calculated. The thermodynamic (theoretical) output data reported in Fig. 3, depict that for values of $S/B \geq 1.5$ wt/wt, the methane production is completely disadvantageous; this would indicate that there are no more carbon elements (coming from hydrocarbons species) left to sustain the increase in the production of CO , CO_2 and H_2 . In other words, the main steam reforming reactions are almost completed resulting in a “syngas composition equilibrium” where the molar fractions remain independent by S/B ratio [39]. Hence, an experimental gasification “blank-no catalyst” test was carried out at 1023 K and $S/B = 1.5$ wt/wt. Results in terms of outlet stream composition (Fig. 4) showed a good match with the thermodynamic data. However, the different approach of the

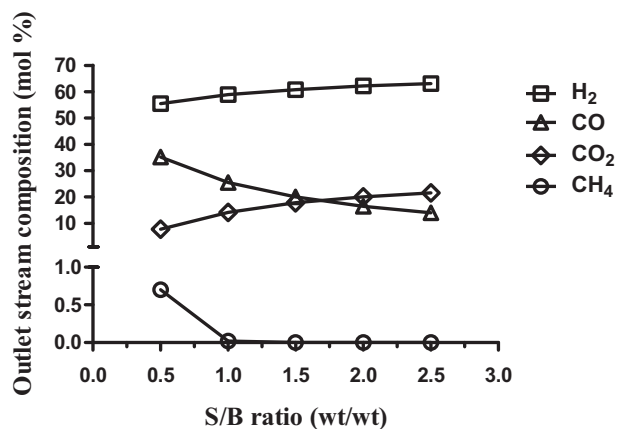


Fig. 3 – Effect of Steam/Biomass ratio on thermodynamic outlet stream composition (1023 K; 1 bar).

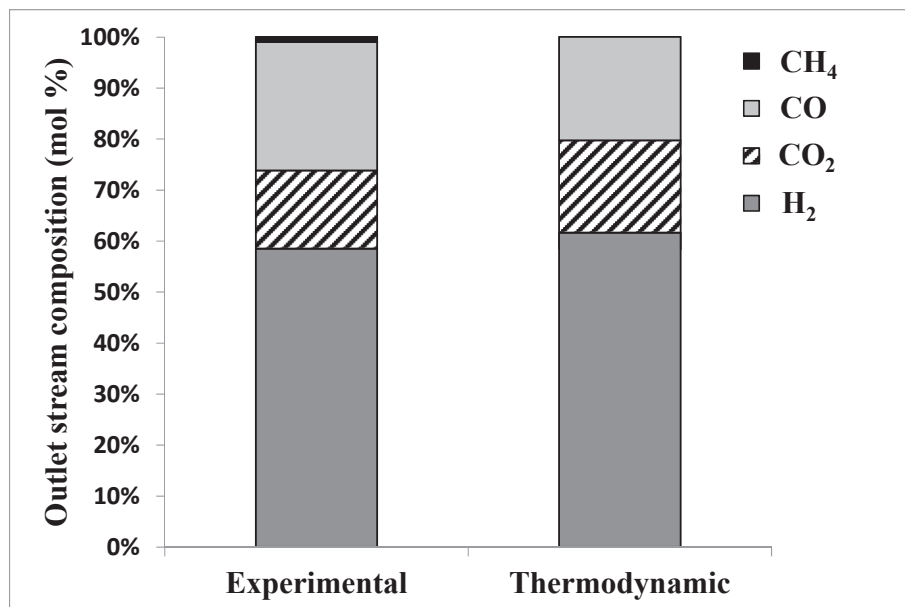


Fig. 4 – Experimental and Thermodynamic data of the outlet stream composition ($T = 1023\text{ K}$; $S/B = 1.5\text{ wt/wt}$).

software simulator to the methane steam reforming equilibrium ($\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}$) under the operative conditions considered (1023 K ; $S/B = 1.5\text{ wt/wt}$) led at a slight CO_2 increasing than experimental conditions (17.8 mol% and 15.4 mol%, respectively); this is due to the gas water shift mass action reaction rate ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$) [40].

To evaluate the effect of catalytic materials on citrus peels steam gasification process, further tests were performed introducing dolomite, MgO and Ni/Al₂O₃ in the thermal reactor.

Results reported in Fig. 5, clearly demonstrate that both CGE and H₂GE rates increased working with catalysts than exclusively citrus residues in the reactor (from 43.7% to 54.9% and from 34.3% to 54.1% for CGE and H₂GE, respectively). Catalytic tests showed very close CGE rates (51.6–54.9%), while from the H₂GE point of view, the dolomite resulted to be the most selective system toward H₂ production (54.1%). This suggest that the catalysts presence probably promote the

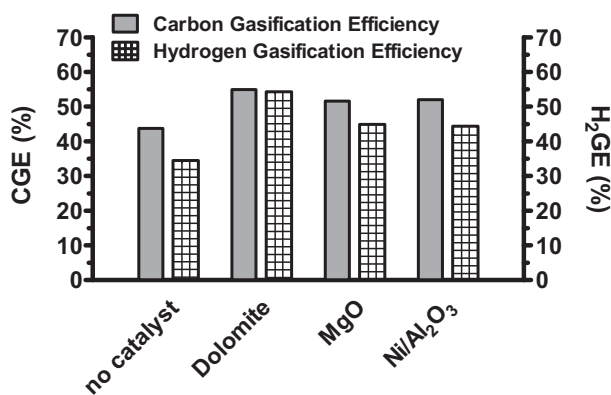


Fig. 5 – CGE and H₂GE rates of citrus peels ($T = 1023\text{ K}$; $S/B = 1.5\text{ wt/wt}$).

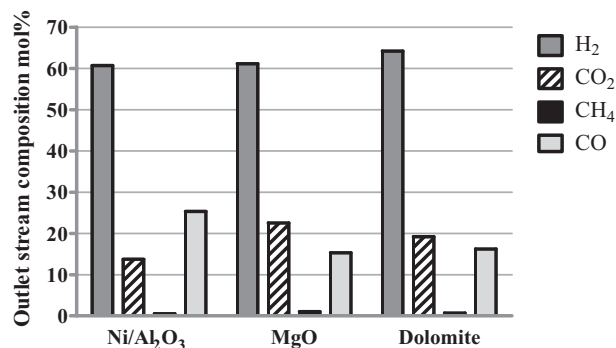


Fig. 6 – Outlet stream compositions of catalytic citrus peels gasification ($T = 1023\text{ K}$; $S/B = 1.5\text{ wt/wt}$).

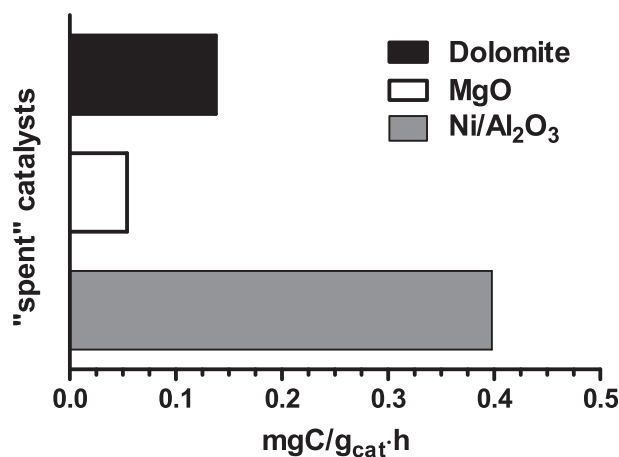


Fig. 7 – Carbon formation rate on “spent” samples catalysts ($T = 1023\text{ K}$; $S/B = 1.5\text{ wt/wt}$).

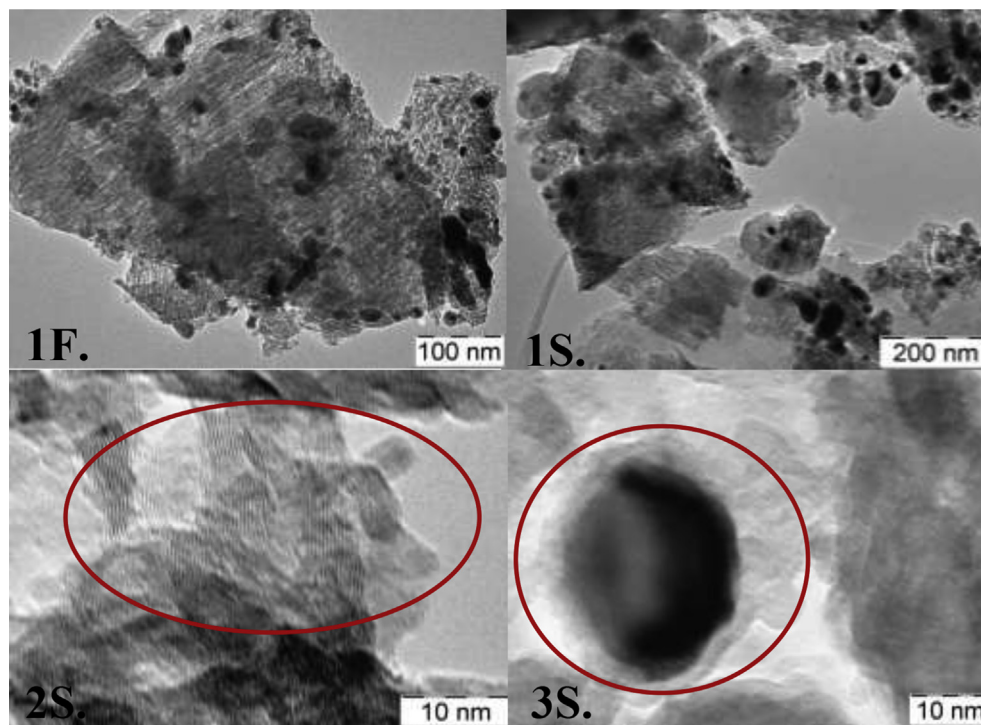


Fig. 8 – TEM images of Fresh (F) and Spent (S) Ni/Al₂O₃ samples catalyst (T = 1023 K; S/B = 1.5 wt/wt).

carbon conversion reactions to gas over tar and char fractions, in agreement with literature where catalysts are able to increase the overall efficiency of the biomass conversion process by 10% [29,41]. In addition, it could be hypothesized that the basicity catalysts properties reduce the yields of light hydrocarbons species (C_xH_y) through the steam reforming reactions (C_xH_y + H₂O ⇌ H₂ + CO), which would promote the H₂ production.

The effect of each catalyst on citrus peels gasification can be also explained considering the outlet stream compositions showed in Fig. 6, where dolomite and MgO depict close selectivity toward H₂ (≥61 mol%) and carbon dioxide (≥18 mol %) species; while experiments performed with Ni catalyst and no-catalyst showed the promotion of CO (about 25.30 mol%) at disadvantage of the CO₂. These data seem to confirm the hypothesis above reported where catalysts and its chemical-physical properties result to have a fundamental role in the yield of syngas through the progression of steam reforming reactions which consequently increase of H₂ and CO₂ production [41–43].

According to the basicity properties of the catalysts can be deduced the following hydrogen production active scale: dolomite > MgO > Ni/Al₂O₃ [41,42]. Hence it should also explain the highest H₂GE rate compared with other catalysts. In this way, the slight lower performance of the MgO catalyst than dolomite in terms both carbon and H₂GE, could be attributed to the lacking of the CaO mineral in the magnesium oxide structure. However, the Ni catalyst appears to have a poor effect on citrus peels gasification (under the investigated experimental conditions), contrary to literature [30].

To shed light on this behavior all “spent” catalysts were analyzed by CHNS elemental analysis (Fig. 7). Results showed that after 2 h of test a significant amount of carbon formation

rate occurs on Ni surface with higher rate (about 0.4 mgC/g_{cat}·h) than that on the other catalysts.

Moreover, TEM micrographs carried out on Ni spent catalyst sample used in the test are shown in Fig. 8. The high magnifications TEM images showed substantial differences between fresh (F) and spent (S) Ni samples catalyst. In particular, spent sample highlighted a growing of metal particles from 11 nm to 50 nm, probably due to sintering phenomena (1S), as observed by calculation reported in Fig. 9. Furthermore, TEM overview at low magnifications of Fig. 8, revealed the formation of both graphitic (2S) and encapsulating (3S) carbon on Ni spent sample.

By comparing results shown in Figs. 6 and 7, it can be concluded that the behavior of the Ni catalyst in the citrus peels steam gasification may have been affected both fouling

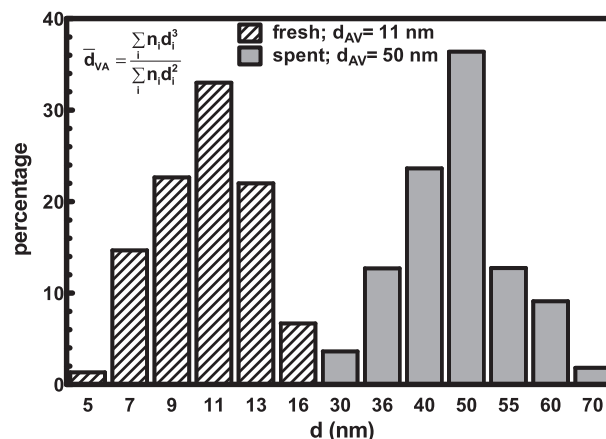


Fig. 9 – Ni Particle distribution from TEM analysis of Fresh and Spent Ni/Al₂O₃ catalyst.

and sintering phenomena; these probably promoted by different factors, as the acidic nature of Al_2O_3 support and the involving of secondary tar reactions which led to coke and tars production [44].

Conclusions

Steam gasification experiments were performed in a fixed bed laboratory-scale reactor in order to evaluate the feasibility to produce H_2 rich syngas from dry citrus peel residues. The results of the thermo-gravimetric analysis showed that in terms of thermal decomposition of the citrus peel moderate gasification temperatures (≥ 1023 K) could be used to convert the residues in syngas working with steam as oxidant ($S/B \geq 1.5$ wt/wt).

It was noticed that under investigated experimental conditions a syngas composition in agreement with thermodynamic equilibrium can be produced. In particular, concentrations of H_2 and CO of 58.80 mol% and 25.34 mol% were recorded, respectively.

From catalytic gasification measurements was observed that both carbon and hydrogen gasification efficiencies can be promoted working with dolomite, MgO and $\text{Ni}/\text{Al}_2\text{O}_3$ in the reactor (from 43.7% to 54.9% and from 34.3% to 54.1% for CGE and H_2GE , respectively).

The dolomite resulted the best catalyst for citrus peels steam gasification under the examined operative condition with CGE and H_2GE rates of 54.9% and 54.1%, respectively. However, the Ni catalyst resulted to be affected by carbon formation and sintering on time on stream.

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