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Enhanced Hydrogen Production by Assisted Biomass Gasification Using Lithium Manganate as Bifunctional Material

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Abstract

The rising energy demand, among other economic and technological factors, increases the greenhouse gas emissions. Therefore, it is crucial to develop technologies to produce clean energy, such as hydrogen ($H_2$) generation from biomass sources. Within this context, using alkaline ceramics reports promising results for pyrolysis and gasification processes. The present study aims to study hydrogen production testing the bifunctional activity of lithium manganate ($Li_2MnO_3$), using glucose and cellulose molecules as biomass models. Furthermore, it is evaluated the heating rate effect, as well as the biomass:ceramic molar ratio. Glucose results show that $Li_2MnO_3$ addition into pyrolysis highly enhances and shifts the $H_2$ production to lower temperatures, through assisted gasification process, reducing $Mn^{4+}$ ions to $Mn^{3+}$ and $Mn^{2+}$. Besides, solid products evidence carbon capture, which mainly contribute to improve the $H_2/CO_x$ ratios. Then, when testing cellulose, at the best glucose:$Li_2MnO_3$ experimental pyrolytic conditions, corroborated the ceramic bifunctional application. Thus, further studies on biomass assisted-gasification process have
significance importance using modified Li-Mn-based ceramics by improving microstructural properties to enhance \( \text{H}_2 \) production and purity while reducing carbon oxides emissions.

1. Introduction

Over the world, energy demand has been rising as result of overpopulation as well as technology development.\(^1\)-\(^3\) Moreover, the dependence to fossil fuels to supply this energy demand has caused a continuous increment of \( \text{CO}_2 \) emissions, which have increased up to 423.7 ppm, causing several and severe health and environmental problems.\(^4\)-\(^6\) Therefore, governments have started focusing on several strategies to mitigate greenhouse gas (GHG) emissions.\(^7\),\(^8\) Within this context, the transition to renewable energy sources seems to be one of the most promising solutions.\(^9\) However, clean energies and alternative fuels have several economic, technological, social and environmental challenges, such as limited accessibility, dependance to weather conditions, low governments funding and the use of engine technologies.\(^10\),\(^11\)

From this perspective, hydrogen based economy has been attracting attention as a potential clean vector fuel, due to its zero emissions and high energy density as well as its diverse production sources,\(^12\),\(^13\) such as methane reforming, water electrolysis, bioproduction, photoelectrochemical water splitting and biomass conversion, among others.\(^14\)-\(^18\) In fact, biomass conversion, by pyrolysis and gasification processes, has been widely recognized as a key process to supply the world energy demand due to its low cost, neutral carbon print increment and local accessibility.\(^19\)-\(^22\)
Biomass feedstock is defined as any organic solid material susceptible to be burned or transformed into end products (modern biomass), such as syngas mixtures (H$_2$+CO), bio-oils and/or bio-char. Conversely, pyrolysis is a thermochemical process in oxygen deficiency, which can be performed from around 250 to 850 °C, producing bio-oils, bio-char and different gaseous products, such as, hydrogen (H$_2$) and carbon oxides (CO$_x$), in addition to other light organic gases. On the other hand, depending on the biomass composition low amounts of sulfur oxides and/or nitrogen oxides could be found. Moreover, gasification is a partial thermal oxidation process, where an oxygen source must be supplied (air, steam, supercritical water and/or CO$_2$). This process is usually carried out at higher temperatures than pyrolysis, being the main product a syngas mixture (H$_2$+CO), as well as CO$_2$, water and gaseous hydrocarbons. However, some low quantities of secondary compounds like tar and char (mixture of carbon or ash) may be produced. 

Even though H$_2$ production from thermochemical conversion of biomass is a neutral CO$_2$ emission process, as it is produced as a syngas, and its application is limited. For instance, to feed fuel cells, to generate electric energy, as they are prone to be poisoned by CO, the H$_2$ supply must go through costly purification techniques, namely cryogenic separation, pressure swing adsorption (PSA), or membrane selective separation, to diminish CO impurities to < 10 ppm. Moreover, it has been reported that the addition of different metal oxides or supported metal-particles as catalysts in addition to CO$_2$ sorbents during the pyrolysis and gasification processes enhance H$_2$ production and increasing its purity.

Within this context, alkaline ceramics have demonstrated high capture capabilities for CO$_2$ and/or bifunctional properties for consecutive process, like CO oxidation and subsequent chemisorption. In fact, Li$_4$SiO$_4$ and Na$_2$ZrO$_3$ have been already reported as
bifunctional catalyst-sorbent materials during the pyrolysis process, enhancing the H₂ production and chemically trapping CO₂ as carbonates.⁴²,⁴³ However, Zr or Si catalytic properties are poor or inexistent. Therefore, the study of different bifunctional ceramics with better catalytic properties for biomass pyrolysis process is crucial.⁴⁴ In this sense, only lithium manganate (Li₂MnO₃) has demonstrated a selective CO catalytic (T < 500 °C) and chemisorption (T ≥ 500 °C, reaction 1, maintaining some catalytic activity) capabilities in inert or non-oxidative conditions.⁴⁵,⁴⁶ Moreover, this material was tested using a synthetic syngas mixture for H₂ purification, reporting a very low ceramic interaction with H₂.⁴⁷

\[
\text{Li}_2\text{MnO}_3 (s) + CO(g) \rightarrow \text{Li}_2\text{CO}_3 (s) + \text{MnO}(s)
\]  

Based on this background, this work aims to analyze the catalytic and sorption effects of Li₂MnO₃ addition during biomass pyrolysis, using glucose and cellulose as model molecules.²⁸,⁴⁸,⁴⁹ This study was performed using a thermobalance and a catalytic flow reactor system, with complementary techniques.

2. Experimental Section

2.1. Synthesis and characterization

Li₂MnO₃ was synthesized by solid state method using manganese (II) oxide (MnO, Meyer) and lithium oxide (Li₂O, Aldrich) as reactants, following previously reported methodology.⁴⁵,⁴⁷,⁵⁰ This methodology involved the mechanical mixing of both powders with a lithium excess of 5 wt%.⁵¹,⁵² The resultant mixture was pelletized (40 MPa) and heat-treated at 900 °C during 12 h in air. Afterwards, the product was pulverized and fully characterized by X-ray diffraction (XRD) and N₂ adsorption-desorption. XRD analysis was
performed at room temperature (RT) using a D5000 diffractometer (Siemens) coupled to a copper anode X-ray tube (Cu Kα-radiation). Prior N₂ adsorption-desorption measurement, the sample was degassed under vacuum at RT for 12 hours. Then, a Minisorp II instrument (BEL Japan) was used to perform the analysis at 77 K. Besides, specific surface area (S_{BET}) was determined using the Brunauer-Emmett-Teller (BET) model.

2.2. Catalytic and carbon oxides sorption measurements

Li₂MnO₃ effect over biomass pyrolysis process was studied. Glucose (C₆H₁₂O₆, Aldrich) molecule was selected as initial model of study. Therefore, different homogeneous Li₂MnO₃:glucose mixtures were prepared (Table 1). Each mixture, labeled as LMO-G, was mechanically mixed in an agate mortar for 10 minutes.

<table>
<thead>
<tr>
<th>Measurement type</th>
<th>Sample label</th>
<th>Li₂MnO₃ (wt%)</th>
<th>Glucose (wt%)</th>
<th>Mass ratio (ceramic/glucose)</th>
<th>Molar ratio (ceramic/glucose)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermogravimetry (Thermobalance)</td>
<td>LMO-G 5-95</td>
<td>5</td>
<td>95</td>
<td>0.0526</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>LMO-G 25-75</td>
<td>25</td>
<td>75</td>
<td>0.3333</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>LMO-G 50-50</td>
<td>50</td>
<td>50</td>
<td>1.0000</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>LMO-G 75-25</td>
<td>75</td>
<td>25</td>
<td>3.0000</td>
<td>0.82</td>
</tr>
<tr>
<td>Gas evolutions (Catalytic reactor)</td>
<td>LMO-G 5-95</td>
<td>5</td>
<td>95</td>
<td>0.0526</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>LMO-G 10-90</td>
<td>10</td>
<td>90</td>
<td>0.1111</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>LMO-G 15-85</td>
<td>15</td>
<td>85</td>
<td>0.1765</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>LMO-G 20-80</td>
<td>20</td>
<td>80</td>
<td>0.2500</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>LMO-G 25-75</td>
<td>25</td>
<td>75</td>
<td>0.3333</td>
<td>0.34</td>
</tr>
</tbody>
</table>

To identify the influence of Li₂MnO₃ over the glucose decomposition behavior, a broader scope of Li₂MnO₃ content (from 5 to 75 wt%) was analyzed thermogravimetry,
including glucose alone, for comparison purposes. These experiments were performed using a Q550 thermobalance (TA Instruments) in an inert atmosphere (flowing 60 mL min\(^{-1}\) of N\(_2\), Praxair grade 4.8) from 30 to 950 °C, at 5 °C min\(^{-1}\). Then, LMO-G 25-75 sample was selected to evaluate the heating rate (HR) influence over the gaseous products, employing a fixed-bed catalytic reactor (Bel-REA, from Bel Japan) attached to a cooler (water trap), a FTIR gas-cell spectrometer (ALPHA-Platinum, from Bruker) and a gas chromatography system (GC-2014 with a Carboxen-1000 column, from Shimadzu). The sample (200 mg) was placed over a quartz wool support and dynamically heated from 30 to 850 °C, using a N\(_2\) flow of 60 mL min\(^{-1}\) at various heating rates (5, 10, 20 and 30 °C min\(^{-1}\)). Additionally, the best obtained conditions (flowing 60 mL min\(^{-1}\) of N\(_2\) with a heating rate of 30 °C min\(^{-1}\)) were selected for evaluating a glucose sample, for comparison purposes. Complementarily, the condensable volatile products from the glucose and LMO-G 25-75 samples were recovered using a cooler system and analyzed through GC-mass spectrometry (GC-MS) (GCMS-QP 2010 SE, from Shimadzu). These samples were diluted in 1 mL of methanol, then an aliquot of 1 μL was injected into the equipment in split mode, using helium (He 4.5 grade, Praxair) as carrier gas and a Rtx®-200 column (Resteck). The mass spectra of this samples were compared with the NIST11 database.

Thereafter, it was evaluated the effect of the Li\(_2\)MnO\(_3\) amount in the ceramic-biomass mixtures over the gaseous products during the biomass pyrolysis. For this purpose, Li\(_2\)MnO\(_3\) content was diminished in the ceramic-glucose mixtures from 25 to 5 wt% (see Table 1).

These experiments were performed in the catalytic reactor system using N\(_2\) (60 mL min\(^{-1}\)) and the best heating rate conditions (30 °C min\(^{-1}\)). Complementarily, to elucidate the effect of lithium presence in the ceramic composition, a sample only containing manganese
(IV) oxide (MnO₂, Meyer) and glucose was evaluated at the best Li₂MnO₃:glucose conditions (25:75, heating rate of 30 °C min⁻¹ in N₂ flow of 60 mL min⁻¹).

Based on all these results, the best heating conditions (30 °C min⁻¹ in N₂ flow) and the best ceramic:biomass ratio (0.3333) were selected to study the whole pyrolysis process involving Li₂MnO₃ and glucose, following a two steps procedure: i) the sample was dynamically heated from RT to the target temperature of the study (between 500 and 700 °C every 50 °C), and ii) the sample was isothermally treated at the target temperature during 2 h. Moreover, all these isothermal solid products as well as the as-prepared mixture (LMO-G 25-75) were characterized by XRD and attenuated total reflectance infrared spectroscopy (ATR-FTIR, ALPHA-Platinum, from Bruker).

After determining the best conditions for glucose pyrolysis (30 °C min⁻¹ and 0.3333 mass ratio of ceramic in N₂ flow), they were used to evaluate the cellulose. Li₂MnO₃ and cellulose ((C₆H₁₀O₅)ₙ, Aldrich). This mixture was mechanically mixed in an agate mortar for 10 minutes (labeled as LMO-C). Then, LMO-C was thermogravimetrically analyzed and tested in a catalytic reactor, as described above. It must be mentioned that all the experiments described above were repeated, at least, three times to evaluate their reproducibility.

2.3. GC data processing

GC data was processed calculating the flow (mL min⁻¹) of each compound from concentration (gas specie flow/total flow) according to eqn. 2, where \( F_x \) is the flow of each gas, \( C_x \) is the concentration of that gas and \( F_T \) is the total flow of each aliquot. The concentration of each compound \( (C_x) \) was determined by calibration curves, which were experimentally determined using different mixtures of N₂ (Infra, grade 4.8), CO (Praxair, 5
% N\textsubscript{2} balanced), CO\textsubscript{2} (Praxair, grade 4.8), H\textsubscript{2} (Praxair, grade 4.5) and CH\textsubscript{4} (Infra, grade 4.8), respectively. On the other hand, the total flow (\(F_T\)) was determined from the concentration and the flow of the inert gas (N\textsubscript{2}) in the analyzed aliquot. Then, the collected flow data was normalized to biomass (glucose or cellulose) content (eqn. 3), where \(F_{N,x}\), \(F_x\) and \(m\) are the normalized flows of each gas, the gas flow in mL min\(^{-1}\) and the biomass mass in gram units, respectively.

\[ F_x = C_x (F_T) \]  
(2)

\[ F_{N,x} = \frac{F_x}{m} \]  
(3)

Moreover, from collected data, the total volume of gaseous products normalized per gram of biomass (\(V\)) were calculated through the integration of the flow normalized data, as a function of time (\(F_{N,x}(t)\), eqn. 4), from initial \(t_0\) and final time \(t_f\).

\[ V = \int_{t_0}^{t_f} [F_{N,x}(t)] dt \]  
(4)

### 2.4. Kinetics parameters calculation

The Flynn-Wall-Ozawa integration method was implemented to calculate the kinetic parameters of glucose and cellulose pyrolysis processes, in presence or absence of Li\textsubscript{2}MnO\textsubscript{3} at a mass ratio of 0.3333. These samples were thermogravimetrically analyzed by modifying the HR from 10 to 30 °C min\(^{-1}\) every 10 °C min\(^{-1}\), using N\textsubscript{2} flow (60 mL min\(^{-1}\)). All collected data were fitted to eqns. 5 and 6, where \(E_a\), \(A\), \(R\), \(\alpha\), \(\beta\), \(T\), \(a\) and \(b\) are Arrhenius activation energy, pre-exponential factor, gas constant, conversion value of decomposition, heating rate, temperature; \(E_a/T\) and \(T/E_a\) numerical integration constants, respectively. \(E_a\) and pre-exponential factor were determined as the average of obtained \(\alpha\) values from 0.08 to 0.13.
3. **Results and Discussion**

Li$_2$MnO$_3$ was synthesized following the methodology previously reported.$^{45,47,50}$ Herein, the data characterization of the material is provided in supplementary information (Fig. S1), in which XRD pattern fitted to 01-081-1953 file from PDF database, corresponding to the monoclinic Li$_2$MnO$_3$ crystal structure, without the presence of any other secondary phase. In addition, N$_2$ adsorption-desorption isotherm depicted an isotherm type II, according to IUPAC classification, without the presence of any hysteresis loop.$^{53,54}$ Besides, a specific surface area ($S_{BET}$) below of 1 m$^2$ g$^{-1}$ was determined. These results are in agreement with previous solid-state synthesis reports for this material.$^{45,46,50}$

After the Li$_2$MnO$_3$ characterization, it was evaluated the effect of its addition into the glucose pyrolysis process, through dynamic thermogravimetric analyses (Fig. 1), where different mixtures of Li$_2$MnO$_3$ and glucose were tested (see Table 1), including a pristine glucose sample. Fig. 1A shows noticeable differences for the expected weight lost, depending on the Li$_2$MnO$_3$:glucose ratios. Indeed, in the pristine glucose case, most of the mass was lost (~77.5 %) in a single and continuous step, between 170 and 550 °C. Afterwards, it slowly lost 4 wt% in the remaining temperature range (550 to 950 °C), where the final solid product was only carbon (C) and ash traces, mixture so-called char.$^{55}$ Conversely, when Li$_2$MnO$_3$ was added not only the temperature in which the process started was reduced, depending on...
the Li$_2$MnO$_3$ amount, but also the process was split into three steps. For instance, after the first weight lost, it was stabilized at 480 °C for LMO-G 5-95, this weight stabilization temperature diminished as a function of Li$_2$MnO$_3$, up to 430 °C for the LMO-G 75-25 sample. Besides, after the weight stabilization, it was depicted a second decomposition process from 580 to 625 °C for LMO-G 5-95 and LMO-G 75-25 samples, respectively. Then, the third weight lost seemed to be stabilized in the samples with 25 and 50 wt% of Li$_2$MnO$_3$, while the samples with lower ceramic content did not reach a plateau zone. Evidently, the final mass lost produced by each sample depends as a function of the glucose content, as Li$_2$MnO$_3$ has been reported as a thermal stable material between RT and 650 °C in a N$_2$ flow.$^{45}$ In fact, during the last decomposition process, it might be involved the superficial oxygen release from the Li$_2$MnO$_3$ crystal structure, being it lower than 1.8 wt% only considering Li$_2$MnO$_3$.$^{45}$

![Fig. 1](image)

**Fig. 1.** (A) Thermogravimetric analyses from mixtures of different Li$_2$MnO$_3$ and glucose ratios at 5 °C min$^{-1}$ in N$_2$ flow. (B) Normalized weight lost percentages to glucose content, compared against the glucose pyrolysis alone (black line at zero position).

To understand the processes involved during the Li$_2$MnO$_3$-glucose pyrolysis, it was determined the expected weight loss of glucose for each sample (Fig. S2). Moreover, all the
thermogravimetric data were treated according to eqn. 7, to determine differences in the weight loss behavior of each sample, in comparison to pristine glucose sample ($\Delta wt\%$). $wt_s\% (T)$ and $wt_g\% (T)$ are the weight percentages of each LMO-G sample and glucose, respectively, as a function of temperature. Moreover, $m_g/m$ and $m_c/m$ are the mass ratio of glucose and ceramic in each LMO-G sample.

$$
\Delta wt\% (T) = wt_s\% (T) - \left( \left[ wt_g\% (T) \cdot \frac{m_g}{m} \right] + \frac{m_c}{m} \right)
$$

(7)

The zero line, in Fig. 1B, represents the glucose behavior during the pyrolysis process (as it was described by eqn. 7). Therefore, negative values between 100 and 270°C can be entirely associated with a catalytic effect during the pyrolysis process, due to the $\text{Li}_2\text{MnO}_3$ addition. This catalytic effect was narrower in temperature range and more evidenced as the ceramic content diminished. On the other hand, positive values (from 250 to 740 °C) must be related with the retained mass that was not released as a gas during the pyrolysis process. It seems that CO and/or CO$_2$ are being chemically sorbed as lithium carbonate ($\text{Li}_2\text{CO}_3$).\textsuperscript{45,47} It must be noticed that the retained amount was higher in the sample with the lowest ceramic content (8.6 wt% for LMO-G 5-95 sample). Moreover, as $\text{Li}_2\text{MnO}_3$ content increased, the lower were the retained gas amounts. It must be taken into account the fact that carbon oxides (CO$_x$) concentrations diminished, simply as a consequence of the lower glucose content. Therefore, it must be modifying the solid-gas interphase, decreasing CO capture, the last evidenced as lower positive mass percentages.\textsuperscript{46} Furthermore, two crest are depicted in this temperature range. The first one (~250 and 440 °C) could be associated to surface CO$_x$ sorption-desorption equilibrium, while the latter (~440 and 740 °C) should involve the CO$_x$
chemical capture controlled by Li$^{1+}$ and O$^{2-}$ diffusion mechanisms,$^{56}$ alongside some thermal stress occurring.$^{57}$

Nevertheless, these positive values can be also attributed to a stabilizing process where other compounds derived from the glucose could be produced, such as bio-oils.$^{58,59}$ Within this approach, it must be noticed, that between 250 and 440 °C, the glucose pyrolysis has not finished, then, as the positive values did not continuously increase, some bio-oils may be also going through several decomposition processes, increasing the gas production.$^{60}$ Whereas, from 440 to 600 °C, most of the pyrolysis decomposition has occurred, implying that bio-oil may be thermally stable at that temperature range. The last observed negative values can be associated to a further decomposition process, Li$_2$CO$_3$ decomposition involving the oxygen loss from the crystal structure (reaction 8), and/or the so-called Boudouard reaction (reaction 9),$^{61-62}$ or a partial carbon oxidation taking oxygen from the crystal structure (reaction 10). In this last step, it is also plausible that Li$_2$MnO$_3$ (or a derived solid) can be reacting with formed bio-oils in a partial oxidation reaction, where the oxygen source comes from the ceramic, decreasing the final produced char. It fits with the negative value observed, in comparison to glucose pyrolysis.

$$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g) \quad (8)$$

$$C(s) + CO_2(g) \rightarrow CO(g) \quad (9)$$

$$Li_2Mn^{4+}O_3(s) + \frac{\delta}{2}C(s) \rightarrow \frac{\delta}{2}CO(g) + Li_2Mn^{4+/3} + O_3 - \delta(s) \quad (10)$$

All these TG analyses suggest the end formation of gaseous compounds during the glucose decomposition. Therefore, the gas evolutions were evaluated using LMO 25-75 sample, in order to figure out the best H$_2$ production conditions. Moreover, HR was modified
from 5 to 30 °C min\(^{-1}\) to enhance gases production\(^{63}\). Glucose pyrolysis produced H\(_2\), CO, CO\(_2\) and CH\(_4\), all of them with different trends depending on the heating rate (Fig. 2). In the H\(_2\) case (Fig. 2A), it was barely produced from 200 to 400 °C. Afterwards, its production significantly increased from 400 to 850 °C, regardless the heating rate. However, as the heating rate increased the flow of H\(_2\) per gram of glucose augmented as well, from 3.2 to 14.8 mL min\(^{-1}\) g\(^{-1}\) glucose when using heating rates of 5 and 30 °C min\(^{-1}\), respectively. Moreover, it can be observed two peaks during H\(_2\) formation, similarly to the two-crest observed in the thermogravimetric analyses (see Fig. 1B). In fact, these two peaks are more evident as a function of the heating rate, and they are observed at higher temperatures than the ones using lower heating rates, perhaps due to a non-equilibrium condition.

Similarly, the HR enhanced the CO\(_2\) production (Fig. 2B), shifting its maximum to higher temperatures; from 2.5 to 9.5 mL min\(^{-1}\) g\(^{-1}\) glucose at 190 and 357 °C, respectively. Moreover, temperature range of CO\(_2\) production (150-600 °C) was also shifted around 80 °C to higher temperatures, when HR was 5 and 30 °C min\(^{-1}\), respectively. It must be noticed that CO\(_2\) was mainly produced at lower temperatures than H\(_2\) production.

On the other hand, CO formation (Fig. 2C) presented an interesting behavior. CO was produced starting at 190 °C up to the end of every dynamic analysis. However, it must be pointed out that this production depicted two crests, being the first between 190 and 500 °C with a maximum production of 3.3 mL min\(^{-1}\) of CO per gram of glucose at 330 °C for the 30 °C min\(^{-1}\) case. It must be noticed that CO production was always lower than CO\(_2\) production within this temperature range. Moreover, it must be pointed out that in the first crest case, the starting CO production temperature was lower than that where Li\(_2\)MnO\(_3\) can chemisorb it (420-705 °C).\(^{45}\) Then, at higher temperatures (525-850 °C), the second crest was observed,
reaching a maximum production at around 700 °C, depending on the ceramic:glucose ratio.

For instance, the maximum CO production was depicted using a HR of 10 °C min⁻¹ at 697 °C (34.7 mL min⁻¹ g⁻¹glucose). Besides, as the HR increased, from 5 to 20 °C min⁻¹, CO production significantly increased, and that crest seems to become broader. However, this trend was not observed when using a HR of 30 °C min⁻¹. Furthermore, the second CO production crest matched with H₂ production. It must be emphasized that within this temperature range Li₂MnO₃ selectively reacts with CO.⁴⁵,⁴⁷ In addition, it must be mentioned that the produced carbon, or any possible bio-oil, must be mainly oxidized to CO₂, as its production is higher than that for CO₂, reducing manganese species. In fact, H. Zhang et al.⁶⁴ reported that MnO₂ could be reduced up to MnO by reacting with volatiles (tar) from biomass pyrolysis, producing H₂, CO and some light carbons. At last, CH₄ production (Fig. 2D) was depicted between 390 and 705 °C. In this case, maximum methane production was also increased and right shifted 100 °C, as a consequence of the increase in the HR, being less than 1 or 4 mL min⁻¹ g⁻¹glucose, for HR of 5 and 30 °C min⁻¹, respectively.
Based on all these results, the best heating conditions seems to be 30 °C min\(^{-1}\), as this condition depicted the higher H\(_2\) production. Thus, for comparison purposes, glucose sample was tested and included in Fig. 2, depicting that the addition of Li\(_2\)MnO\(_3\) not only highly enhances the H\(_2\) production but also decreased its starting production (Fig. 2A). For instance, in absence of ceramic, the best H\(_2\) production was 6.9 mL min\(^{-1}\) g\(^{-1}\) glucose at 717 °C. Moreover, Li\(_2\)MnO\(_3\) addition seemed to modify the carbon oxides production. In the CO case (Fig. 2C), in presence of Li\(_2\)MnO\(_3\) the temperature range of CO production was shifted 80 °C to lower temperatures. Furthermore, its addition modified the CO production in two different stages.
The first stage, between 410 and 615 °C, the CO production was lower in presence of Li₂MnO₃, matching with the temperature range of CO capture in Li₂MnO₃. Despite of this phenomenon, in the second stage (T > 615 °C), the CO production was increased twice in Li₂MnO₃ presence. This must be explained due to the oxygen release from the crystal lattice which oxidize the glucose pyrolysis byproducts, diminishing the available oxygen. Moreover, Boudouard reaction should be occurring due to CO₂ production from carbonate decomposition and as intermediate from the CO oxidation-capture. Additionally, in the CO₂ case (Fig. 2B), Li₂MnO₃ addition increased the overall production and left shifted the maximum CO₂ production, in comparison to pristine glucose. This is also a consequence of CO oxidation produced by Li₂MnO₃. Then, in CH₄ case (Fig. 2D), the glucose sample depicted a broader temperature range production, suggesting that Li₂MnO₃ addition inhibits CH₄ formation.

Complementarily, all the gaseous products were analyzed through a FTIR gas-cell (Fig. S3). For instance, CO vibration bands are observed at 2120 and 2170 cm⁻¹, whereas CO₂ vibration bands are depicted at 670, 2350, 2360, 3600, 3630, 3700 and 3740 cm⁻¹. Moreover, it was evidenced the water formation (1500, 1700, 3400 and between 3670 and 3850 cm⁻¹ bands), regardless the implemented heating rate. Furthermore, some vibration bands associated to C-H bonds were identified between 1400 and 1800 cm⁻¹ as well as at 2950 cm⁻¹, all of them different from methane vibration bands (1300 and 3010 cm⁻¹). Hence, some bio-oils or organic compounds must be produced during the pyrolysis, which are described as a mixture of aldehydes, ketones, phenols, aromatic compounds, heterocyclic compounds, among others. Indeed, in the present case, the recovered bio-oils from the LMO-G 25-75 and glucose dynamic experiments at 30 °C min⁻¹ were identified as mixtures
of these compounds. These identifications were performed by chromatography coupled to mass spectrometry (Fig. S4).

To further understand the HR effect over the gases production, H\textsubscript{2}/CO ratio was calculated as a function of the temperature (Fig. 3A) Fig. 3A shows that, in presence of Li\textsubscript{2}MnO\textsubscript{3}, the H\textsubscript{2}/CO ratio increased in two different stages, between 430 and 580 °C and after 720 °C. In the first stage, the H\textsubscript{2}/CO ratio was not larger than 11.3 for HR of 5, 10 and 20 °C min\textsuperscript{-1}. However, at 30 °C min\textsuperscript{-1}, the H\textsubscript{2}/CO ratio was 40.0 at 532 °C. Afterwards, for all Rs, the H\textsubscript{2}/CO ratio diminished significantly (around 0.10 at 700 °C), reaching a second increment stage at 800 °C (between 2 and 3.3). These results show that using a HR of 30 °C min\textsuperscript{-1} highly increases the H\textsubscript{2}/CO ratio. The increase of HR must induce a higher CO capture. Indeed, CO\textsubscript{x} partial pressure decrement may compromise its capture by modifying the solid-gas interphase.\textsuperscript{66–69} Furthermore, through comparing the H\textsubscript{2}/CO ratio with the one obtained in the glucose case, it depicted a considerably decrement and right shift, being 4.3 at 615 °C. Consequently, the addition of Li\textsubscript{2}MnO\textsubscript{3} in the pyrolysis process did not only increase the H\textsubscript{2} production, but also enhanced its purity.
Additionally, in consideration of the whole process, in Fig. 3B the amounts of all produced gases were plotted. In the H₂ case, it is shown that the total amount of H₂ was not importantly affected (variations lower than 11 %) by heating rate, being 134.1 mL g⁻¹ glucose at 5 °C min⁻¹ and 122.7 mL g⁻¹ glucose at 30 °C min⁻¹. It must be mentioned that dynamic experiments depicted higher H₂ production flows at high HR (see Fig. 2A), although the production over the time was similar. This phenomenon must be related to the pyrolysis kinetics, as the heating rate increased, the glucose was pyrolyzed faster preventing to reach an equilibrium over the respective gaseous products. This trend suggests that at certain temperatures different products were obtained in higher amounts, although final equilibrium over the H₂ production must be limited by thermodynamics or by the specific path of pyrolysis decomposition when Li₂MnO₃ was added to the process.

On the other hand, thermodynamic equilibriums over CO and CO₂ productions were highly affected by the HR, after Li₂MnO₃ addition. For instance, CO productions were 339.9 and 270.0 mL g⁻¹ glucose at 10 and 5 °C min⁻¹. Conversely, CO productions diminished at higher heating rates, being 254.1 and 111.2 mL g⁻¹ glucose at 20 and 30 °C min⁻¹, respectively. These results suggest that at low heating rates (5 and 10 °C min⁻¹), the interaction between Li₂MnO₃ and biomass induced a higher release from the oxygen of the crystal lattice structure. These implications, between the two lowest HR, also induced a reduction over the oxygen available for the CO₂ formation, evidenced by a CO₂ reduction from 105.8 to 88.2 mL g⁻¹ glucose at 5 and 10 °C min⁻¹, respectively. Parallely, at HRs of 20 and 30 °C min⁻¹, the CO amounts considerably diminished as well as CO₂ amounts were ~28.7 % lower. In fact, at 30 °C min⁻¹, the total CO and CO₂ amounts were 111.2 and 76.8 mL g⁻¹ glucose, respectively. Besides,
CH$_4$ formation was increased as a function of HR, from 8.5 to 15.5 mL g$^{-1}$ glucose at 5 and 30 °C min$^{-1}$, respectively, apart from the HR of 10 °C min$^{-1}$, which would be associated to the large selectivity from glucose pyrolysis to CO. Based on these results, HR increment must kinetically enhance oxygen release as well as induce CH$_4$ formation. Moreover, as a reason of non-equilibrium conditions, at higher HRs, the material must be achieving high temperatures faster than the CO release from the pyrolysis process, favoring the CO capture.

Moreover, whole H$_2$/CO$_x$ ratios were evaluated at the different heating rates (Fig. 3B). These results depicted that the best ratios were observed using a HR of 30 °C min$^{-1}$. Conversely, other HR conditions depicted similar H$_2$/CO and H$_2$/CO/(CO+CO$_2$) ratios; around 0.5 and 0.36. Moreover, H$_2$/CO$_2$ ratios were similar for all the HR (around 1.59) except for the HR at 5 °C min$^{-1}$ (1.26).

Then, by comparing the gas amounts from LMO-G 25-75 with those from pristine glucose, it is evident that H$_2$, CO and CO$_2$ amounts were larger in Li$_2$MnO$_3$ presence. In fact, ceramic addition increased in 1.8 times the H$_2$ and CO amounts, while increasing 1.6 times the CO$_2$ amount. Meanwhile, Li$_2$MnO$_3$ addition decreased CH$_4$ formation. Complementarily, the H$_2$/CO and H$_2$/CO$_x$ ratios for the glucose sample were not so different in comparison to the obtained for the LMO-G 25-75 sample. In the H$_2$/CO$_2$ case, it was incremented due to Li$_2$MnO$_3$ addition, mainly for the increment in the H$_2$ production. All these results indicate that Li$_2$MnO$_3$ modifies the mechanism of glucose pyrolysis, enhancing H$_2$ production and inducing carbon oxides formation, but significantly increasing the H$_2$/CO ratio within a specific temperature range (430–580 °C), while diminishing other hydrogenated compounds (H$_2$O, CH$_4$ and tar).
Based on all the previous experiments, the heating rate of 30 °C min\(^{-1}\) was selected to further study the Li\(_2\)MnO\(_3\) effect over the pyrolysis process. Thus, different LMO-G mixtures were prepared, where glucose amounts were increased (Table 1). H\(_2\), CO, CO\(_2\) and CH\(_4\) flows, normalized per gram of glucose, are presented in Fig. 4. As it can be observed, Li\(_2\)MnO\(_3\) content increased H\(_2\) production (Fig. 4A), from 8.3 to 14.2 mL min\(^{-1}\) g\(^{-1}\) glucose at 532 °C, for 5 and 25 wt% of Li\(_2\)MnO\(_3\), respectively. This trend must be related to an increase of the surface contact between glucose and Li\(_2\)MnO\(_3\), enhancing the selectivity of glucose decomposition towards H\(_2\).

On the other hand, carbon oxides production depicted slight differences depending on Li\(_2\)MnO\(_3\) content. In the CO\(_2\) case, it was produced from 122 to 840 °C, reaching a maximum at around 225 °C (Fig. 4B). It must be noticed that CO\(_2\) productions were shifted to higher temperatures for 5 and 25 Li\(_2\)MnO\(_3\) wt% samples. In fact, the 5 wt% sample was shifted to 327 °C due to low Li\(_2\)MnO\(_3\) content. This temperature is closer to peak CO\(_2\) production temperature in the glucose sample case (410 °C). On the other hand, the 25 wt% sample was shifted to 357 °C, as part of CO\(_2\) produced comes from CO oxidation. These data show that low amounts of ceramic tend to behave similarly to the gas evolution of glucose decomposition, as it could be expected.

In addition, during the CO production (Fig. 4C), again it depicted two different behaviors, depending on the ceramic content. In the first CO production trend (between 225 and 430 °C), as the ceramic content diminished, the higher the CO production. Contrarily, on the second CO production thermal range, CO production augmented inversely to the Li\(_2\)MnO\(_3\) percentage. These phenomena must be intertwined, as a function of CO oxidation-capture and oxygen availability during pyrolysis, as both processes are favored with
Li$_2$MnO$_3$. However, as the oxygen availability increases, Li$_2$MnO$_3$ capabilities to react with some byproducts are increased. On the other hand, it is also plausible that CO production during the second thermal process was augmented due to higher lithium carbonate production, which reacts with char.

In the CH$_4$ case, samples with 10, 15 and 20 wt% of Li$_2$MnO$_3$ depicted shifts to lower temperatures and diminished the productions. Moreover, all of them produced lower CH$_4$ amounts than glucose. In a previous work, it was evidenced that CH$_4$ formation is not favored by Li$_2$MnO$_3$ when H$_2$ and CO are present. Hence, this result implies that CH$_4$ formation from glucose pyrolysis is mainly related to carbon oxides formation. In fact, methane formation must be favored once the available oxygen diminished. Moreover, as CH$_4$ formation increased in samples with higher H$_2$ production, a methanation process (reaction 11) must be involved.

\[ 2 \text{H}_2(\text{g}) + \text{C}(\text{s}) \rightarrow \text{CH}_4(\text{g}) \]  

(11)
Fig. 4. Thermal evolution of the produced gases ((A) H$_2$, (B) CO$_2$, (C) CO and (D) CH$_4$) for LMO-G and MnO$_2$-G samples, from 30 to 850 °C in N$_2$, using a heating rate of 30 °C min$^{-1}$. All of them normalized per gram of glucose.

Complementarily, it becomes keystone to elucidate the lithium effect, determining if described behaviors were only related to a manganese catalytic effect, or to lithium properties too. It must be mentioned that lithium oxide (Li$_2$O) was not complementarily tested due to its high corrosivity and toxicity levels, which would discourage its use. Hence, MnO$_2$ was evaluated in the same conditions where the highest H$_2$ production was obtained (25 wt% of ceramic content and a HR of 30 °C min$^{-1}$). This sample was labeled as MnO$_2$-G 25-75. Fig. 4 shows that using MnO$_2$ conserved the H$_2$ production thermal range, but decreasing its production and concentration, in comparison to Li$_2$MnO$_3$-containing samples. Conversely, CO production depicted a triple peak behavior, being the first slightly lower than the observed
for the LMO-G 25-75 sample. The second peak showed a significantly higher CO production at 532 °C, in comparison to all the Li$_2$MnO$_3$-containing samples. Then, the third CO production peak fitted in temperature with the second peak of the Li$_2$MnO$_3$-containing samples, being the CO production lower in the MnO$_2$ case. It must be mentioned that, in comparison to LMO-G 25-75, the CO$_2$ production of the MnO$_2$-G sample was higher at T \leq 225 °C, but it became lower, between 252 and 532 °C, increasing again at higher temperatures.

In the MnO$_2$-G case, CO and CO$_2$ behaviors seem to be intertwined, as the CO$_2$ production was higher at low temperatures (T \leq 225 °C), probably due to an increase of the surface’s oxygen availability. Conversely, as the temperature increased (from 252 to 532 °C) the surface’s oxygen availability may be decreasing, diminishing CO oxidation. Moreover, as MnO$_2$ does not exhibit the CO$_x$ capture capabilities, CO production was higher than that using Li$_2$MnO$_3$. Then, at higher temperatures (T > 532 °C), a carbon source (char or tar) and/or CO are oxidized to CO$_2$ through the core oxygen lattice of MnO$_2$.

In the CH$_4$ case, the implementation of MnO$_2$ diminished the methane production, but its formation temperature range fitted with the highest H$_2$ and CO formations. It must be noted that in presence of any Mn$^{4+}$ source, namely MnO$_2$ or Li$_2$MnO$_3$, the methane formation was lower in comparison to glucose sample. Consequently, the reaction pathway of carbon oxides formation induces H$_2$ production, both modifying CH$_4$ formation. Indeed, CO$_x$ production leaded to low methane and carbon formations. However, the H$_2$ production increments and high temperatures in carbon presence induced a weak methanation reaction.$^{70,71}$ Based on all these results, it is indirectly determined that lithium presence,
within the Li$_2$MnO$_3$ crystal structure, does promote higher H$_2$ productions, of course producing CO$_x$ capture, which resulted in better H$_2$/CO$_x$ selectivity.

For comparison purposes, Fig. 5 shows the overall gases production normalized to gram of glucose for all the LMO-G samples. The total amount of H$_2$ was significantly increased with the augmentation of Li$_2$MnO$_3$ content, from 69.2 to 122.7 mL g$^{-1}$glucose. Moreover, the sample with the lowest content of Li$_2$MnO$_3$ (LMO-G 5-95) produced a similar H$_2$ amount than that of glucose sample (around 69.6 mL g$^{-1}$glucose), as it would be expected. On the other hand, MnO$_2$-G produced only 79.4 mL g$^{-1}$glucose, being significantly lower than Li$_2$MnO$_3$ with the same mass content, indicating that the Li-based ceramic does present improvements over H$_2$ production.

As it can be observed, LMO-G and MnO$_2$-G samples showed higher CO and CO$_2$ productions, in comparison to pristine glucose. Furthermore, when carbon oxides production of MnO$_2$-G and LMO-G (both at 25 wt%) are compared, it can be observed that CO and CO$_2$ productions of the LMO-G sample were lower, in 37.4 and 4.4 %, respectively. All these results show that Li$_2$MnO$_3$ contents, even if the H$_2$ production is not dramatically enhanced, diminish the overall carbon oxides production during the glucose pyrolysis.

Lastly, in the CH$_4$ case, it diminished from 11.9 to 7.8 mL g$^{-1}$glucose for LMO-G 5-95 and LMO-G 15-85 samples. Afterwards, it increased up to 15.5 mL g$^{-1}$glucose for the LMO-G 25-75 sample. Besides, the MnO$_2$-G sample produced lower CH$_4$ amounts (12.0 mL g$^{-1}$glucose) than LMO-G 25-75 sample. It must be noticed, regardless the manganese source and weight content, CH$_4$ amount was always lower than the obtained from the glucose sample. Hence, the hydrogen available, from glucose, to produce CH$_4$ is reduced, modifying the reaction pathways in which glucose decomposes.
Fig. 5. Total volume of the gaseous products from pyrolytic processes of the LMO-G, MnO$_2$-G and glucose samples, all of them normalized per gram of glucose (bottom and left axes), as well as H$_2$ and carbon oxides ratios obtained as a function of the molar ratio (top and right axes).

In addition, Fig. 5 shows the overall H$_2$/CO$_x$ ratios as a function of the molar fraction of Li$_2$MnO$_3$, depicting that the highest H$_2$/CO ratio (1.45) was observed for the sample with the lowest proportion of ceramic (LMO-G 5-95, $X_{Li_2MnO_3} = 0.08$). At high Li$_2$MnO$_3$ contents, H$_2$/CO ratios were not so high, reaching a minimum at 0.21 molar content (15 wt% of ceramic) and increasing again with the ceramic content. This trend must be related to the capability of Li$_2$MnO$_3$ to release some oxygen at high temperatures (T > 700 °C),$^{45}$ inducing the partial oxidation of the carbon species to CO, during the glucose pyrolysis. This statement is supported by the previous dynamic experiments, where CO was mainly produced over 650 °C (see Fig. 4C). On the other hand, the H$_2$/CO$_2$ ratios depicted an interesting behavior as a function of the ceramic’s molar fraction. At a ceramic’s molar fraction of 0.08, the H$_2$/CO$_2$ was slightly higher in comparison to the glucose sample (1.50 and 1.40, respectively). molar fraction of 0.15, the H$_2$/CO$_2$ decreased to 0.99. Then, further Li$_2$MnO$_3$ contents tended to
increase the H$_2$/CO$_2$ ratio, up to 1.60. Finally, the H$_2$/(CO+CO$_2$) ratio displayed a similar trend than that of H$_2$/CO$_2$. As it was previously discussed, carbon oxides formation must be intertwined with ceramic contents, favoring the CO oxidation-capture process.

Based on all previous sections, LMO-G 25-75 sample was selected for performing dynamic-isothermal experiments. Fig. 6 shows a dynamic-isothermal description of the gaseous products, performed between 500 to 700 °C. Herein, most of the gaseous products were mainly obtained during the heating process, such as H$_2$, CO$_2$ and CH$_4$. H$_2$ production (Fig. 6A) in all these cases started at the sixth minute ($T \geq 240$ °C), reaching its maximum at the respective target temperature. It must be noticed that H$_2$ production was mainly produced during the initial 31 min, and after that, its production decreased to around 0.5 mL min$^{-1}$ g$^{-1}$, regardless the isothermal target. Moreover, as all these measurements were carried out fixing different isothermal temperatures, the best H$_2$ production was obtained in the isothermal performed at 500 °C, in well-agreement with the dynamic experiments.

In the CO case (Fig. 6B), three production peaks are observed at 240, 500 and 700 °C. Moreover, the lowest CO productions were observed at around 400 and 600 °C. It must be noticed that these CO production are presented within the same temperature ranges where Li$_2$MnO$_3$ oxidize and chemically trap CO.$^{45}$ On the other hand, CO production significantly diminished after ~20 min of the isothermal step. It must be pointed out that, at the highest temperatures, CO production was observed after H$_2$ productions had finished, showing that Li$_2$MnO$_3$ was reacting with one of the products of the glucose pyrolysis, for instance char, inducing the Mn$^{4+}$ partial reduction.

Complementarily, the main CO$_2$ production (Fig. 6C) was observed after 3 minutes ($T \geq 130$ °C), reaching a maximum at 240 °C. Then, CO$_2$ production significantly decreased
as a function of temperature and time, becoming negligible after 24 min. It must be mentioned that below 450 °C, CO\textsubscript{2} production was larger than that of CO. Perhaps, glucose thermal decomposition is shifted to water and carbon dioxide formation at moderate temperatures ($T \leq 450$ °C), due to its large oxygen content. Additionally, CH\textsubscript{4} production (Fig. 6D) was observed after the initial 10 minutes ($T \geq 340$ °C), reaching a maximum at around 500 °C (15.6 min). Inversely, to H\textsubscript{2} results, CH\textsubscript{4} formation was negligible once the isothermal target temperatures were reached, indicating a weak methanation process.\textsuperscript{70,71}

![Fig. 6. Thermal and time gas evolutions of; H\textsubscript{2} (A), CO (B), CO\textsubscript{2} (C) and CH\textsubscript{4} (D) for LMO-G 25-75 sample, during different dynamic-isothermal processes performed between 500 and 700 °C, normalized per gram of glucose. Spheres and solid lines](image_url)
represent gas flows as a function of temperature and time. For easier visualization two projections were done, flow as function of temperature (triangles and dotted lines) and temperature as function of time (shadowed circles).

Fig. 7 depicts the overall gases production and $\text{H}_2/\text{CO}_x$ ratios depending on the isothermal target temperatures, before starting isothermal steps (Fig. 7A) and after the whole processes (Fig. 7B). In fact, all the overall gases production increased as a function of temperature (Fig. 7A). Specifically, in the experimental sections reaching 500 and 700 °C, $\text{H}_2$ and CO production amounts depicted the highest increments. In the $\text{H}_2$ case, these values increased from 19.7 to 90.3 mL g$^{-1}$glucose, whereas, in the CO case, from 17.7 to 54.2 mL g$^{-1}$glucose. It must be noticed that although CO$_2$ production increased as a function of temperature, these increments were not higher than 13 % among them, ranging from 81.7 to 91.9 mL g$^{-1}$glucose between 500 and 700 °C. Again, as it has been explained, most of the CO$_2$ production occurred below 430 °C. On the other hand, CH$_4$ production merely increased from 7.4 to 11.1 mL g$^{-1}$glucose, at reaching 500 and 700 °C, respectively. So, CH$_4$ formation did not really change as a function of the initial step, the dynamic process.

Additionally, Fig. 7A shows the $\text{H}_2/\text{CO}_x$ ratios once the target temperature was reached. All the $\text{H}_2/\text{CO}_x$ ratios increased as a function of final dynamic temperature, except for the $\text{H}_2/\text{CO}$ ratio at the highest final dynamic temperature. In the $\text{H}_2/\text{CO}$ case, it increased from 1.22 at 500 °C to 1.97 at 650 °C, diminishing to 1.75 at 700 °C. This sudden change, in the CO increment, is related to the oxygen release from Li$_2$MnO$_3$, which is produced at high temperature, as already described. On the other hand, the $\text{H}_2/\text{CO}_2$ ratio increment trend (from 0.28 at 500 °C to 1.04 at 700 °C) must be related to the fact that CO$_2$ is mostly produced at low temperatures ($T < 430 ^\circ$C). In contrast, when both carbon oxides are considered ($\text{H}_2/\text{CO}_x$ ratio), it equally increased with temperature, from 0.23 at 500 °C to 0.65 at 700 °C, as it is simply the addition of the two previous cases. Based on these results, it would be of interest
to avoid collecting gases below of 500 °C, to diminish the CO₂ and CO contents in 88.9 and 32.7 %, respectively, even though it would diminish the H₂ amount in 21.8 % during the dynamic heating process reaching 700 °C.

Fig. 7B show the gases production once the whole processes were completed, including isothermal sections. It can be noticed that H₂ amounts significantly increased, in comparison to the dynamic heating steps, for example 90.3 and 144.3 mL g⁻¹glucose at the experiment performed at 700 °C, before and after the isothermal step. In fact, it corresponds to an increment of 59.9 %. These results indicate that some of the pyrolytic glucose byproducts decomposed during isothermal steps and/or because of the pyrolysis process continued at the target temperature. Likewise, isothermal steps enhanced the CO amounts, depicting a relevant behavior. For instance, in the experiments performed isothermally at 500, 550 and 600 °C the CO production were 36.3, 94.1 and 113.7 mL g⁻¹glucose, respectively. Afterwards, it diminished to 107.6 and 108.9 mL g⁻¹glucose for isothermals steps performed at the two highest temperatures (650 and 700 °C). All these CO productions are larger than those observed during dynamic heating steps. So, during isothermal steps, Li₂MnO₃ promoted reactions with pyrolytic byproducts through the oxygen release. Conversely, the CO₂ productions only increased in around 6.5 % after isothermal processes, in comparison to those produced during dynamic heating steps. Thus, oxygen release, from the material, mostly produced CO. Finally, CH₄ production was almost the same (differences lower than 3.3 %), regardless the isotherm temperature. Therefore, methane is produced in the same amount from the glucose pyrolysis as long as the process is carried out at \( T \geq 500 \) °C, due to weak methanation reaction.
Complementarily, the whole H$_2$/CO$_x$ ratios, including dynamic and isothermal steps, are shown in Fig. 7B. The H$_2$/CO$_2$ ratio is the only one increasing with temperature, from 0.82 at 500 °C to 1.51 at 700 °C. This phenomenon must be related to the poor CO$_2$ production during the isothermal step, in comparison to the enhanced H$_2$ production. On the other hand, H$_2$/CO ratio diminished from 1.94 up to 0.96 at 500 and 600 °C. Then, H$_2$/CO ratio increased again up to 1.33 at 700 °C. In the experiments performed isothermally at 650 and 700 °C, the ceramic was capable to CO capture faster and more efficiently than in the lower isothermal experiments, even though CO production was increased as well during these isothermal tests. In the H$_2$/CO$_x$ case, its value was around 0.55 in the experiments between 500 and 650 °C, slightly increasing to 0.71 at 700 °C. This trend was clearly marked by the larger CO production, in comparison to the CO$_2$ amounts, more than for H$_2$ concentrations.

Fig. 7. Total volume of the gaseous products from dynamic-isothermal process (bottom and left axes) of LMO-G 25-75 sample, between 500 and 700 °C, after the heating dynamic steps (A) and after the whole processes (B), all of them normalized per gram of glucose. Corresponding H$_2$ and carbon oxides ratios are presented as a function of the target temperature (top and right axes).

Complementarily, to identify the solid evolution as a function of temperature, dynamic-isothermal solid products were recovered and characterized by XRD and ATR-FTIR (Fig. 8). From the XRD results (Fig. 8A), it can be observed that glucose signals were
not detectable in either of the solid products. Conversely, Li$_2$MnO$_3$ evolved as a function of the isothermal temperature. At 500 °C, Li$_2$MnO$_3$ seems to be the main crystalline phase, although other crystal phases were detected; $t$-LiMnO$_2$, Li$_{1+x}$Mn$_{2-x}$O$_4$, o-LiMnO$_2$ and MnO, evidencing the partial reduction of Mn$^{4+}$ ions (Li$_2$MnO$_3$) to Mn$^{3+}$ (LiMnO$_2$) and Mn$^{2+}$ (MnO). Furthermore, the presences of $t$-LiMnO$_2$ and spinel Li$_{1+x}$Mn$_{2-x}$O$_4$ are in agreement with the superficial activation of Li$_2$MnO$_3$. Nevertheless, at $T > 500$ °C, Li$_2$MnO$_3$ was not detected, but LiMnO$_2$, MnO and Li$_2$CO$_3$, the last confirming the COx chemical capture. Furthermore, at $T \geq 650$ °C, it was identified the formation of Li$_2$O as well as MnO, and the presence of SiO$_2$ (quartz wool used as support in the implemented reactor). Complementarily, FTIR spectra of the same solid products are presented in Fig. 8B. The vibration bands observed for this sample were assigned as follow: 3800–3000 cm$^{-1}$ to OH stretching, 2960–2860 cm$^{-1}$ to CH stretching, 1880–1590 cm$^{-1}$ to C=O stretching, 1525–1345 cm$^{-1}$ to COC (ester) and COH (alcohol) deformations, 1165–965 cm$^{-1}$ to CO and CC stretching, and 860–590 cm$^{-1}$ to CH out-plane vibrations. Moreover, it was identified for all the dynamic-isothermal products the presence of carbonates (vibration bands at 1500-1400 and 800 cm$^{-1}$), confirming the formation of carbonates, for instance Li$_2$CO$_3$. In fact, Li$_2$CO$_3$ was detected in all the samples, even in those where they were not clearly identified by XRD. Furthermore, all the samples depicted a vibration band from 2392 to 2297 cm$^{-1}$, assigned as environmental CO$_2$. All these results corroborate that Li$_2$MnO$_3$ is capable to trap CO$_x$, while it chemically evolves. Only at 500 °C Li$_2$MnO$_3$ acts as catalyst, while in the other temperatures it catalyzes and reacts to CO$_x$. Li$_2$MnO$_3$ to LiMnO$_2$ evolution must contribute to the limited CO capture, as the latter has slower kinetics. Moreover, it was identified the partial reduction of Mn$^{4+}$ to Mn$^{3+}$ and Mn$^{2+}$, with the corresponding oxygen release, evidencing that H$_2$ production increment is due to a partial gasification reaction rather than a catalytic effect over the pyrolysis process.
The following reactions for the glucose pyrolysis are proposed, in absence and presence of Li$_2$MnO$_3$ (reactions 12, 13, 14 and 15), based on the thermogravimetric, chromatographic, XRD and infrared analyses.

$$C_6H_{12}O_6(s) \rightarrow 0.56 H_2(g) + 0.49 CO(g) + 0.40 CO_2(g) + 0.14 CH_4(g) + d H_2O(l) + C_{2.0}H_{10.32} - 2d O_{4.71} - d (l) + 2.97 C(s)$$

(12)

In the glucose pyrolysis, in absence of ceramic (reaction 12), the assigned coefficients of all the gas compounds were determined by GC (see experimental section). The carbon (C) coefficient was determined by the final weight observed during the dynamic TG results (see Fig. 1A), as only carbon is expected to be formed due to the high temperature reached (850
°C). It must be mentioned that this proposal was made in consideration of the qualitative identification of water (observed in the cooler and by FTIR). On the other hand, bio-oils determined by GC–mass spectrometry (Fig. S4) were not quantified. Therefore, it was proposed an unknown organic compound 

\[
C_{2.00}H_{10.32}O_{4.71} - 2d
\]

representing this bio-oils mixture, to adjust this equation by introducing the coefficient factor “d”, for water and for this unknown organic compound.

Likewise, for the reaction proposal of glucose pyrolysis in \( \text{Li}_2\text{MnO}_3 \) presence (reactions 13, 14 and 15), some considerations must be noticed. In this case (LMO-G 25-75 sample), the reaction proposal was made at different temperatures due to differences in the gas phase composition and solid products. The first reaction, for the dynamic-isothermal process performed at 500 °C (reaction 13), the second for the dynamic-isothermal process performed at 700 °C (reaction 14) and the last for the whole dynamic process up to 850 °C (reaction 15).

\[
\begin{align*}
C_6H_{12}O_6(\text{s}) + 0.51 \text{Li}_2\text{MnO}_3(\text{s}) &\rightarrow 0.56 \text{H}_2(\text{g}) + 0.29 \text{CO}(\text{g}) + 0.69 \text{CO}_2(\text{g}) + 0.10 \text{CH}_4(\text{g}) + d \text{H}_2\text{O}(\text{l}) + C_{4.92 - h - w - \delta w}H_{10.48 - 2d}O_{4.84 - d} + w(0.51 - w)\text{Li}_2\text{MnO}_3(\text{s}) + (w(1 - 2\delta))\text{MnO}(\text{s}) + h \text{C}(\text{s}) \quad (13) \\
C_6H_{12}O_6(\text{s}) + 0.51 \text{Li}_2\text{MnO}_3(\text{s}) &\rightarrow 1.16 \text{H}_2(\text{g}) + 0.88 \text{CO}(\text{g}) + 0.77 \text{CO}_2(\text{g}) + 0.10 \text{CH}_4(\text{g}) + d \text{H}_2\text{O}(\text{l}) + C_{4.25 - h - w}H_{9.28 - 2d}O_{4.09 - d - 2w} + h \text{C}(\text{s}) + (0.51 - w)\text{Li}_2\text{O}_2(\text{s}) + w \text{Li}_2\text{CO}_3(\text{s}) + 0.51 \text{MnO}(\text{s}) \quad (14) \\
C_6H_{12}O_6(\text{s}) + 0.51 \text{Li}_2\text{MnO}_3(\text{s}) &\rightarrow 0.99 \text{H}_2(\text{g}) + 0.89 \text{CO}(\text{g}) + 0.62 \text{CO}_2(\text{g}) + 0.12 \text{CH}_4(\text{g}) + d \text{H}_2\text{O}(\text{l}) + C_{4.37 - h}H_{9.54 - 2d}O_{4.38 - d} + h \text{C}(\text{s}) + 0.51 \text{Li}_2\text{O}(\text{s}) + 0.51 \text{MnO}(\text{s}) \quad (15)
\end{align*}
\]

In all these cases, gas products (H\(_2\), CO, CO\(_2\), and CH\(_4\)) were determined by GC, while solid products were identified by XRD or ATR-FTIR. It must be explained in detail that the coefficient factor “w” is related to lithium content in the solid products. Thus, it must not be higher than 0.51 mol. In addition, to adjust reactions, it was proposed an unknown.
organic compound $C,H,O$, which represents the bio-oils. Here, the coefficient factors “h”, “w” and “d” are related to C, H and O relationship in the different gaseous and solid compounds to fit the reaction. Conversely to the glucose case, carbon coefficients were not fitted to thermogravimetric analyses due to the oxidation of this specie by the oxygen from the Li$_2$MnO$_3$ framework or through a reaction with lithium carbonate. Then, at 500 °C, as Li$_2$MnO$_3$ was identified as well as the solid products (see Fig. 8A), it was proposed this activated crystal phase as Li$_2$MnO$_{3-\delta}$. Conversely, at 700 and 850 °C, considering that all the manganese cations (Mn$^{4+}$) must be reduced at the end of the pyrolysis process into Mn$^{2+}$, MnO must exhibit the same molar proportion to LMO-G 25-75 sample (0.51 mol of manganese).

Based on all previous results, this study was expanded. Li$_2$MnO$_3$ was tested for the cellulose pyrolysis, using a mass ratio of ceramic of 0.3333 (or 25 wt%, sample labelled as LMO-C). Fig. 9 shows the dynamic thermogravimetric analyses of LMO-C and cellulose samples at 30 °C min$^{-1}$ in N$_2$ flow (60 mL min$^{-1}$). In the cellulose case, it can be seen two different weight loss (steps), the first one depicted from 70 to 140 °C (around 1.0 wt%), attributed to water evaporation. Then, most of the mass was lost (\~83.2 wt%) in a single and continuous step, similar to the glucose behaviour but at higher temperatures (between 230 and 415 °C). At $T > 415$ °C, cellulose sample slowly lost 6.4 wt%, being final solid product char. In contrast, in Li$_2$MnO$_3$ presence, the process was apparently modified from two steps into three well-defined steps. Indeed, the initial weight lost is merely the dehydration process described above. Then, second thermal step was slightly shifted (\~15 °C) to lower temperatures. This weight loss slowly diminished until stabilized, from 560 to 650 °C. Thus, after that weight stabilization, it was depicted a third decomposition process from 650 to 820
°C. All these behaviors are similar to the observed as consequence of addition of Li$_2$MnO$_3$ to glucose pyrolysis, suggesting similar processes during the glucose and cellulose pyrolysis, namely the catalytic function (second decomposition step), the CO capture (second stabilized zone) and oxygen release from the crystal structure (third decomposition step).

Therefore, data was treated according to eqn. 7, to determine the differences in the weight loss behavior of LMO-C sample in comparison to the expected weight loss of pristine cellulose (the latter represented as the zero line in Fig. 9B). Obtained trend is similar to that observed for the LMO-G samples, so the phenomena involved during the cellulose pyrolysis must be closely related. In this case, the negative values between 215 and 408 °C are entirely associated to a catalytic effect during the pyrolysis process due to Li$_2$MnO$_3$ addition. On the other hand, the positive values (from 408 to 800 °C) depicted the same two crests, related to CO and/or CO$_2$ chemical capture as Li$_2$CO$_3$ and/or to the formation of some bio-oils thermally stable within this temperature range. Besides, the last negative values (between 803 and 950 °C) are related to the oxygen release from the crystal structure.

![Thermogravimetric analyses from cellulose mixture with Li$_2$MnO$_3$ or without it, at 30 °C min$^{-1}$ in N$_2$ flow (A). Normalized weight lost percentages to cellulose content (B), compared against the cellulose pyrolysis alone (black line at zero position). Glucose and LMO-G 25-75 results were added in the panel (A) for comparison purposes.](image-url)
Additionally, LMO-C and cellulose samples were catalytically tested. Fig. 10 shows the gases evolutions normalized to cellulose content. H₂ production was carried out from 225 to 900 °C, being always higher in Li₂MnO₃ presence, mostly between 225 and 532 °C, where a maximum of 10.9 mL min⁻¹ was depicted. In fact, this amount is significantly lower as well as shifted to lower temperatures than those the observed for the LMO-G case. CO₂ production presented an interesting behaviour, which was significantly lower (23.9 mL min⁻¹) in presence of ceramic in comparison to pristine cellulose (43.0 mL min⁻¹). It must be noticed that CO₂ production is depicted in a higher but narrower temperature range than those of glucose cases. From T > 440 °C, CO₂ production diminished, but being always higher in Li₂MnO₃ presence. Besides, at 635 °C it was shown a second local maximum, which may be associated to CO oxidation-capture process.

CO production depicted a similar behaviour in presence or absence of Li₂MnO₃ from room temperature to T < 532 °C. Particularly, at 532 °C, CO production was lower for LMO-C, then it increased up to 800 °C. This trend is in well-agreement with the previous discussion presented above for the LMO-G cases. Thereby, temperature increment not only activates the CO capture process, but also the oxygen release from the ceramic structure, increasing CO and CO₂ productions. Here, as the CO production increased, from 635 to 800 °C, CO₂ production diminished, indicating that a fraction of CO₂ was captured. However, it must be emphasized that the CO production at T < 400 °C was larger in the cellulose sample, whereas at T > 600 °C, it was larger in the glucose case, explained below. In the CH₄ case, it was produced from 372 to 737 °C, being in general slightly smaller in presence of ceramic. In comparison to glucose cases, CH₄ production temperature range was broader for cellulose.
pyrolysis and it does not fit with high H₂ and CO productions. Thus, CH₄ formation may be mainly because of the cellulose decomposition mechanism.

It must be mentioned that the differences in the gas evolutions observed for the cellulose case must be closely related to the presence of the O-glycosidic bonds, modifying the H₂ production to lower temperatures, while increasing the carbon oxides formation at T < 400 °C. Moreover, the lower hydroxyl groups contents reduce the water production probability. Therefore, oxygen atoms within the cellulose polymer are prone to produce the most thermodynamically stable compound (CO₂).

In consideration of the whole process, the overall amounts of the produced gases were plotted while normalized per gram of biomass (Fig. 10E). As it can be observed, cellulose pyrolysis produces high H₂, CO and CO₂ amounts, while CH₄ decreases. Thus, the O-
glycosidic bond highly modify the decomposition mechanism. Moreover, Li₂MnO₃ addition, in both types of biomasses, induces larger amounts of H₂ and CO, being smaller the effect on cellulose, although its H₂ and CO amounts are higher. Conversely, CO₂ amount diminished for the LMO-C sample in comparison to pristine cellulose, although it is, again, higher than that on glucose. Similarly, Li₂MnO₃ addition diminished the CH₄ in both biomass samples. Hence, the addition of Li₂MnO₃ enhances H₂ production by an assisted gasification process, inducing the oxidation of biomass to CO and CO₂, being partially captured as Li₂CO₃. Moreover, the O-glycosidic bonds modify the mechanism of carbon oxides formation. Based on all these results, cellulose decomposition reactions, in Li₂MnO₃ absence or presence, were proposed (reactions 16 and 17), following the same methodology as glucose-containing samples, considering water and bio-oils formations, the last represented as CₓHᵧOₜ, where “x”, “y” and “t” vary depending on the gaseous and solid products. Moreover, coefficient factors “d” and “h” were added to fit the reaction.

\[
(C₆H₁₀O₅)ₙ(s) \rightarrow n \\
(0.73 \text{ H}_2(g) + 1.08 \text{ CO}_g(g) + 1.25 \text{ CO}_2(g) + 0.10 \text{ CH}_4(g) + d \text{ H}_2\text{O}(l) + C_{2.17\text{H}_8\text{O}_{1.42} - 2d\text{O}_{1.42} - d(l) + 1.40 C(s)) \]
\]

(16)

\[
(C₆H₁₀O₅)ₙ(s) + 0.46 \text{ Li}_2\text{MnO}_3(s) \rightarrow n \\
(0.98 \text{ H}_2(g) + 1.18 \text{ CO}_g(g) + 1.09 \text{ CO}_2(g) + 0.09 \text{ CH}_4(g) + d \text{ H}_2\text{O}(l) + C_{3.64 - h\text{H}_7\text{O}_{2.1} - d(l) + h C(s)} + 0.46 \text{ Li}_2\text{O} + 0.46 \text{ MnO})
\]

(17)

Taking into account all this information, the kinetic parameters of glucose and cellulose pyrolysis were determined by Flynn-Wall-Ozawa integration method, in presence or absence of Li₂MnO₃ (Fig. S5 shows the TG of each experiment). As it would be expected, decomposition activation energy is higher for the cellulose-containing samples (Table 2), attributed to the polymer stability generated through O-glycosidic bonds. In fact, the difference between glucose and cellulose activation energies (32.9 kJ mol⁻¹) matches with the Gibbs energy difference reported by Y. Noshimura et al. (33.18 kJ mol⁻¹). Moreover,
ceramic addition does diminish the pyrolysis activation energy, in both biomasses, confirming all the catalytic and carbon oxides sorption properties described above. Complementarily, H$_2$/CO$_x$ ratios were also calculated, which were also enhanced for both biomass types by Li$_2$MnO$_3$ addition. In addition, it is observed that H$_2$/CO$_x$ ratios of cellulose-containing samples are lower in comparison to glucose-containing ones, simply because of larger carbon oxides formation.

Table 2. Kinetics parameters, H$_2$ to carbon oxides ratios, H$_2$ yield and selectivity of glucose and cellulose pyrolysis processes in presence or absence of Li$_2$MnO$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$ (kJ/mol)</th>
<th>Ln A</th>
<th>$H_2$/CO$_x$ ratio</th>
<th>$H_2$/CO$_2$ ratio</th>
<th>$H_2$/($CO+CO_2$) ratio</th>
<th>H$_2$ yield (%)</th>
<th>H$_2$ selectivity$^a$ (%)</th>
<th>H$_2$ selectivity$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>64.7 ± 1.4</td>
<td>12.3 ± 0.3</td>
<td>1.15</td>
<td>1.41</td>
<td>0.63</td>
<td>9.32</td>
<td>27.40</td>
<td>54.80</td>
</tr>
<tr>
<td>LMO-G</td>
<td>61.0 ± 1.2</td>
<td>13.5 ± 0.3</td>
<td>1.10</td>
<td>1.60</td>
<td>0.65</td>
<td>16.45</td>
<td>30.14</td>
<td>60.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.33$^c$</td>
<td>1.51$^c$</td>
<td>0.71$^c$</td>
<td>19.35$^c$</td>
<td>33.28$^c$</td>
<td>66.55$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.94$^d$</td>
<td>0.82$^d$</td>
<td>0.58$^d$</td>
<td>9.42$^d$</td>
<td>26.21$^d$</td>
<td>52.43$^d$</td>
</tr>
<tr>
<td>Cellulose</td>
<td>97.6 ± 0.5</td>
<td>17.2 ± 0.1</td>
<td>0.68</td>
<td>0.58</td>
<td>0.31</td>
<td>14.62</td>
<td>15.01</td>
<td>30.03</td>
</tr>
<tr>
<td>LMO-C</td>
<td>94.4 ± 2.9</td>
<td>17.1 ± 0.6</td>
<td>0.83</td>
<td>0.89</td>
<td>0.43</td>
<td>19.48</td>
<td>20.66</td>
<td>41.31</td>
</tr>
</tbody>
</table>

$^a$H$_2$ yield was calculated as: H$_2$ yield = (mol of produced H$_2$ / Max mol of H$_2$ from reactions 18 and 19)*100

$^b$H$_2$ selectivity was calculated as: H$_2$ selectivity = (mol of produced hydrogen / mol of all gaseous carbon species)*(carbon for hydrogen ratio)*100

Carbon for hydrogen ratio in H$_2$ selectivity was calculated as: mol of ideal gaseous carbon species / mol of ideal hydrogen, being 0.5 for a (reactions 18 and 19), and 1.0 for b (reactions 20 and 21) calculations.

$^c$Calculated values corresponding to generated data from dynamic-isothermal process at 700 °C.

$^d$Calculated values corresponding to generated data from dynamic-isothermal process at 500 °C.

H$_2$ yield was calculated in consideration of ideal H$_2$ productions from glucose and cellulose; reactions 18 and 19 where it was only proposed the carbon and CO$_2$ formations or reactions 20 and 21 involving exclusively the CO formation. As it can be noticed, cellulose depicted ~1.6 times higher H$_2$ yields than glucose (Table 2), attributed to its lower hydroxyl groups contents prone to be released as water. Furthermore, Li$_2$MnO$_3$ additions increased H$_2$
yields in 1.8 and 1.3 times, in comparison to glucose and cellulose samples, respectively. It
must be generated due to a catalytic effect on carbon oxides formation, diminishing the
available oxygen in the sample to produce water in addition to the ceramic atypical
properties, conferring a preferential reaction with carbon species than with hydrogen species.

\[
C_6H_{12}O_6(\text{s}) \rightarrow 6 H_2(\text{g}) + 3 CO_2(\text{g}) + 3 C(\text{s}) \quad (18)
\]

\[
(C_6H_{10}O_5)_n(\text{s}) \rightarrow n (5 H_2(\text{g}) + 2.5 CO_2(\text{g}) + 3.5 C(\text{s})) \quad (19)
\]

\[
C_6H_{12}O_6(\text{s}) \rightarrow 6 H_2(\text{g}) + 6 CO(\text{g}) \quad (20)
\]

\[
(C_6H_{10}O_5)_n(\text{s}) \rightarrow n (5 H_2(\text{g}) + 5 CO(\text{g}) + C(\text{s})) \quad (21)
\]

Last, but not least, H$_2$ selectivity was estimated as a function of each biomass (Table 2). Similarly to H$_2$/CO$_x$ ratios, cellulose-containing samples depicted lower H$_2$ selectivities
than the glucose-containing samples, merely because of larger amounts of produced gaseous.
As it was mentioned, O-glycosidic bonds on cellulose modified the reaction pathway.
However, Li$_2$MnO$_3$ additions increased the H$_2$ selectivities for both biomasses pyrolysis
processes, due to catalytic and sorption properties, as already explained. It should be
mentioned that Table 2 included the dynamic-isothermal data from glucose pyrolysis was
added, for comparison purposes. From there, it can be observed that these processes depicted
lower H$_2$/CO ratio as the temperature increased. Moreover, the obtained H$_2$ yield and
selectivity at 500 °C was almost the same that the obtained for glucose pyrolysis, but the last
shifted to 350 °C. Obviously, as temperature increased, H$_2$ and CO productions increased,
diminishing H$_2$/CO ratio while increasing H$_2$/CO$_2$ ratio, H$_2$ yield and H$_2$ selectivity.

4. Conclusion
Summarizing, Li$_2$MnO$_3$ was studied as bifunctional material (catalytic and sorption), testing its activity in the biomass pyrolysis process, using glucose and cellulose. Heating rate and molar ratio effects were studied as variables, evidencing that the best H$_2$ production performance was depicted at 30 °C min$^{-1}$ and a Li$_2$MnO$_3$/glucose molar ratio of 0.34. Besides, it was demonstrated that the addition of Li$_2$MnO$_3$ to glucose, during the pyrolysis process, enhances H$_2$ production as well as carbon oxides formation through a gasification process, in which the Li$_2$MnO$_3$ is partially reduced to other crystal structures. Furthermore, it was corroborated the partial chemical capture of the produced CO as Li$_2$CO$_3$ by XRD and FTIR. However, CO chemical capture was not as high as in previous reports, mainly due to low CO partial pressure. On the other hand, at $T \geq 635$ °C, the Boudouard reaction occurred as well as the carbon gasification, due to Li$_2$CO$_3$ decomposition and oxygen release from Li$_2$MnO$_3$, diminishing H$_2$ purity. Finally, when cellulose was tested, data showed not so different results than those obtained in the glucose case. O-glycosidic bonds, present in cellulose, modify the mechanism of carbon oxides formation, enriching H$_2$ production but reducing its purity. Moreover, kinetics analyses showed that Li$_2$MnO$_3$ addition diminishes the activation energy of all these processes, while increasing the H$_2$ yields and selectivities. Based on this whole analysis, it seems that Li$_2$MnO$_3$ is a promising material to be further studied for H$_2$ production from biomass sources through assisted gasification process.

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References


