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Co-production of active char and hydrogen from Algerian Date Palm Spikelet: Matter and energy balance based on experimental data.

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1 Abstract

Hydrogen is increasingly considered as one of the key energy carriers of the future, particularly for decarbonizing high-emission sectors such as industry and transportation. However, its current production remains largely dependent on fossil resources. The main barriers to the economic development of hydrogen production from biomass lie in the cost of the raw material and the complexity of the process, particularly due to the presence of tars in the resulting synthesis gas and the relatively low resale value of hydrogen.

This study aims to investigate the potential of co-production of activated carbon and hydrogen from waste derived from date palm (*Phoenix dactylifera L*) cultivation in North Africa. The proposed process is relatively simple and involves two main stages: the production of char via pyrolysis and its physical activation using steam. The pyrolysis gases are converted into heat by combustion to supply both the process itself and an external heating network, while the gases from the activation stage which are rich in hydrogen and low in tar, are used for hydrogen production after separation.

It has been demonstrated that the proposed process can produce between 30 and 38 g of hydrogen and between 50 and 113 g of activated carbon per kilogram of dry biomass, depending on the operating conditions, while also generating heat equivalent to 38 - 41% of the initial energy content of the biomass. The very low tar content in the activation gases ensures improved performance and extended lifetime of hydrogen purification systems compared to conventional biomass gasification processes commonly reported in the literature.

Keywords: *Pyrolysis; Activation; Biomass; Hydrogen production; Matter balance; Energy balance.*

Nomenclature

DPS	Date Palm Spikelet
DPSC	Date Palm Spikelet Char
DPSAC	Date Palm Spikelet Activated Carbon

DPSAC60	Date Palm Spikelet Activated Carbon 60% of burn-off
DPSAC70	Date Palm Spikelet Activated Carbon 70% of burn-off
DPSAC80	Date Palm Spikelet Activated Carbon 80% of burn-off
LHV	Low Heating Value
HHV	High Heating Value

2 Introduction

Woody biomass is used for time immemorial to supply heat for human being. It's today the first renewable energy resource [1,2] . World increasing energy demand and climate changes because of greenhouse effect makes research into the development of innovative renewable energies and on decarbonization of human activities unavoidable.

One way of achieving these ambitious targets is to use hydrogen as an energy carrier, particularly in the transport sector and for lowering industry carbon intensity [3]. Although the combustion of hydrogen does not produce CO₂ as such, its production, mainly through steam methane reforming, does. An alternative method to steam methane reforming is water electrolysis, but this time the CO₂ emissions are induced by the production of electricity if it is not of renewable origin.

Biomass gasification is therefore considered a promising alternative for producing this energy carrier [4]. Different gasifying agents exist, such as air, steam or a mixture of oxygen and steam. In the first case, the reaction can take place in a dense fluidized bed reactor under autothermal conditions, but the gas produced is diluted in nitrogen, and the hydrogen content obtained is not sufficient to feed the purification systems needed to produce pure hydrogen. In the second case, there is no problem of dilution with nitrogen, but the endothermic nature of the reaction requires the use of a dual fluidized bed [5], which is a complex technology whose economic viability remains uncertain and is likely only for large-scale installations. The last option compensates for the shortcomings of the first two, since it is autothermal, can be carried out in a simple dense fluidized bed and there is no problem with dilution of the gas in the nitrogen. Nevertheless, the gas produced contains a mixture of CO, H₂, CO₂, CH₄ and H₂O as well as significant quantities of tar. To separate the hydrogen from this mixture of gases, different methods are envisaged: membrane purification [6], TSA (temperature swing adsorption) [7] and PSA (pressure swing adsorption) [8]. These methods require the gases to be cleaned beforehand in order to significantly reduce the tar content, which could adversely affect the performance and lifespan of the purification systems. This involves intermediate stages (partial oxidation reactor, condensers, catalytic cracking reactor, steam reforming) that make the process more complex and limit its economic benefits. In addition, the hydrogen concentration in the syngas can reach up to 40%, depending on conditions, still needs to be optimized by using intermediate reactors to promote the water gas-shift reaction (an exothermic reaction), which will consume some of the energy

contained in the gas. The economic interest of this approach has already been discussed [4,9], but remains highly sensitive to the price of the input material.

The main obstacles to the economic development of hydrogen production from biomass are therefore the cost of the raw material and the complexity of the process, particularly due to the presence of tars in syngas, as well as the low resale cost of hydrogen.

One possible way of addressing these issues is to combine hydrogen production with activated carbon one. These high added-value materials, which can exceed of €2,500 per ton in market value, could make the process viable. There are different methods for producing this material, the so-called 'chemical' activation and 'physical' activation methods are commonly used. The latter is a relatively simple two-stage process using simple technologies such as rotary kilns.

The first consists of pyrolysis, which leads to the production of a combustible gas and a coal, while the second consists of the gasification of the coal produced under CO_2 or steam. In the first case, the gas produced contains mainly CO (Boudouard reaction $C + CO_2 \rightarrow 2CO$) whereas in the second, the gas produced contains mainly hydrogen ($C + H_2O \rightarrow CO + H_2$) as well as CO and CO_2 , the CO_2 being produced by the water gas-shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). The tar content in the gases from the activation stage is poorly documented in the literature, but as tars are mainly produced during pyrolysis, it is logical to expect that their content is fairly low and does not require a cleaning stage prior to the hydrogen separation stage.

To further enhance economic feasibility, there is still the possibility of using low-cost biomass compared with wood. The use of biomass waste can drastically reduce the cost of the raw material, but it is often associated with additives that will lead to the production of pollutants (NH_3 , HCN, HCl, H_2S) that will also have to be eliminated and will require the addition of further stages to the process, which will be all the more complex and all the less cost-effective.

Nevertheless, some biomass waste remains compositionally similar to untreated or 'clean' biomass, in particular that which has not been subjected to the addition of polluting additives such as glues, finishing products (paint) and preservatives.

The aim of this work is therefore to study the joint production of hydrogen and activated carbons (by physical activation with steam) from waste products from date cultivation in Algeria, precisely, in Ghardaïa, in particular the date palm spikelet presents in large quantities and little used today. This plant i.e. *Phoenix dactylifera L.* is widely cultivated in the North African and Middle East and countries. More than 70% of the global date palm production are produced in these countries [10], and approximately six million tons per year of by-products are collected [11]. The date palm wastes were used to fabricate carbons based on date palm bark [12], palm date stones [13], mixture (petiole, rachis and fiber) [14], date palm tree fronds [15], date palm petioles [16], date palm seed [17], date palm coir [18] and date palm rachis [19,20].

This article offers novelty through several distinct contributions:

Firstly, there are very few articles dealing with the matter and energy balances of activated carbon production processes. Furthermore, to the best of our knowledge, no article in the literature deals with the co-production of activated carbons and hydrogen. The aim of this work, which is designed to demonstrate the benefits of co-production of activated carbons and hydrogen from biomass waste available in abundant quantities (date palm spikelet) by means of matter and energy balances based on reliable experimental data (no simulation), is therefore highly innovative and could serve as a basis for the design and optimization of processes incorporating the joint production of two high added-value materials.

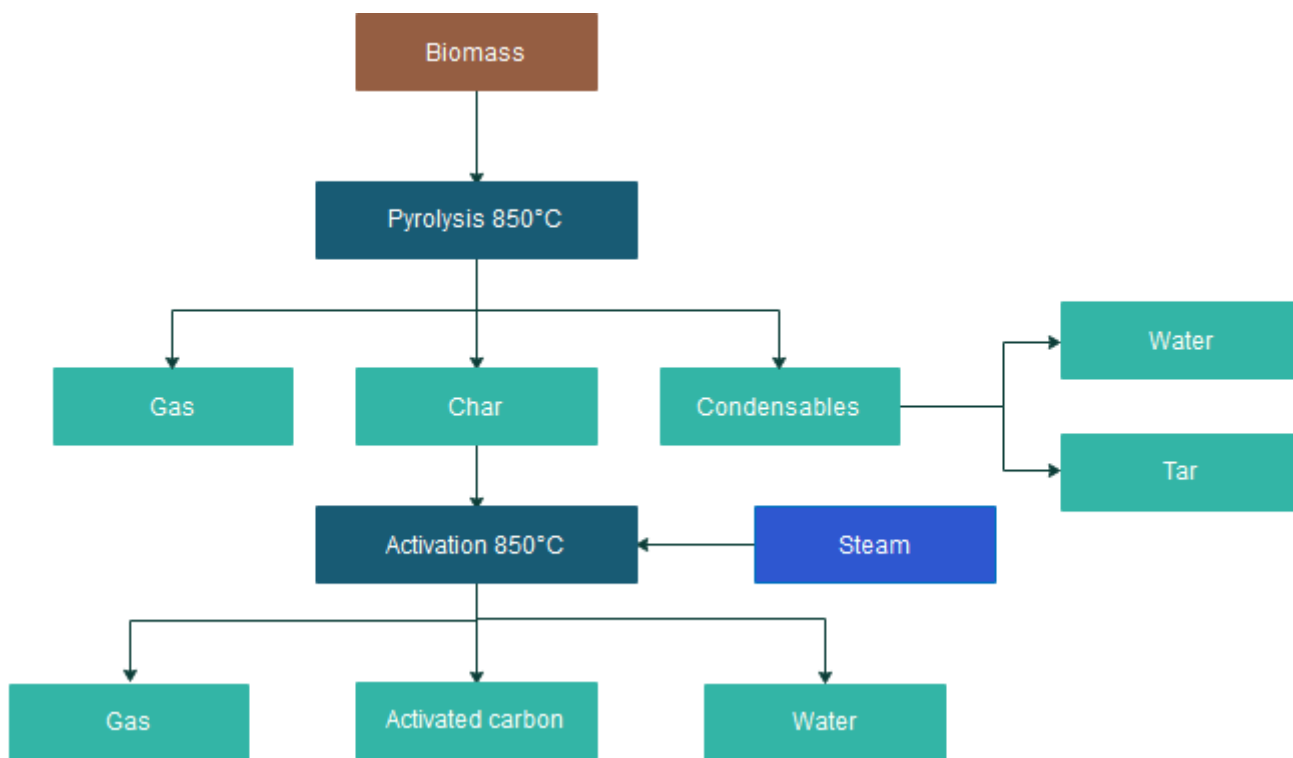


Figure 1 : Scheme of a biomass to energy and activated carbon process

3 Materials and methods

3.1 Biomass preparation

The biomass (date palm spikelet) was obtained from a palm grove in the south of Algeria, exactly, in At Izgen, Ghardaïa province after the date harvest season. The bunch of the date palm was dried in dry air in order to remove the maximum of water contained in the agricultural by-product. Then, the spikelet was cut into small pieces measuring 2 cm. The biomass was dried in an oven at 105 °C for 24 hours. Figure 2 illustrates the date palm bunch and its spikelets.



Spikelet after
collection season



Spikelet prepared
for valorization



Spikelet after
Pyrolysis - Activation

Figure 2 : Pictures of the bunch date palm and Associated Spikelets.

3.2 Experimental apparatus and procedure of pyrolysis and activation process

The pyrolysis – activation experiments (Figure 3) were realized in a rotative stainless-steel tubular reactor placed within an electric horizontal furnace. The device contains:

- A first oven (1123 K) used to preheat the carrier gas and to generate the steam for activation step. Carrier gas (Nitrogen) flow is controlled by a numerical mass flow meter (5 standard L/min for pyrolysis and 3.5 standard L/min for activation step). Water is sent to steam generator using a peristaltic pump. The weight of the water being continually measured by an electronic balance to measure the water flow introduced.
- A rotary tubular reactor (around 50 L) electrically heated by a second oven (1123 K). The rotation speed of the reactor is around 1 revolution per minute. Some lugs are placed inside the reactor to assume a good mixing of the material (improvement of the homogeneity of the activation process). The end of the tubular reactor is throttled to maintain the material in the heated zone.
- A motor attached to the furnace and a drive system to ensure the rotation of the tubular reactor.
- A hot container in 316 stainless-steel, with a capacity of 5 liters, equipped with a passage with a rotating joint for the gas outlet pipe and two connections for the introduction and extraction of biomass or char. This container is equipped with heating mantle.
- A cold container in 316 stainless-steel for loading and unloading, with a capacity of 5 liters, equipped with a gas diffuser.
- A heated flexible line (maintained at 623 K) to transfer gases from pyrolysis/activation reactor to gas cleaning system.
- A gas cleaning system consisting in 3 heat exchangers in series connected to 3 bottles to collect the condensable (water + tars) at the outlet of the reactor. Heat exchangers are supplied by a cold-water flow (2 °C) produced by a cryostat.
- A particle filter which contains cotton wool, dry sawdust, and silica gel was placed at the outlet of the reactor to trap any residual condensable and clean the flow of the gases resulting from the

process. The system was connected to a micro-GC (μ GC, Agilent 490) to analyze the generated gases (N_2 , H_2 , CO , CO_2 , CH_4 , C_2H_4 , and C_2H_6) during this process.

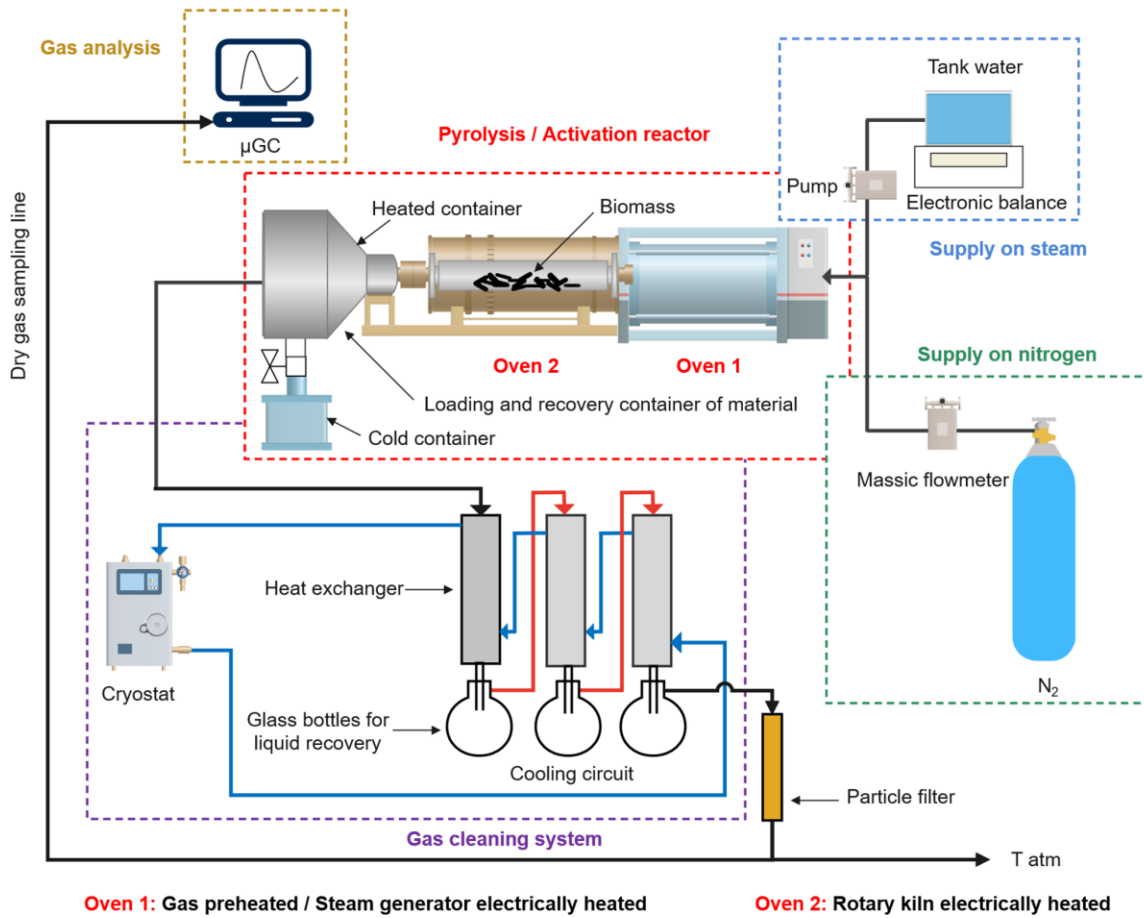


Figure 3 : Scheme of the pyrolysis/activation reactor.

The pyrolysis test was conducted under consistent conditions; 350 g of dried biomass was introduced into this reactor under nitrogen flow rate of 5 NL/min. After an inert phase of 5 min, the temperature of the reactor was increased from ambient temperature to reach a temperature of 1123 K with a rate of 10 K/min. At the end of the pyrolysis step, condensable trapped in the bottles of the cleaning system was removed and weighed. Then, the activation step was started by introducing a flow of steam until the determined burn-off was attained. Gases produced during both steps were continually analyzed by micro gas chromatograph. At the end of the reaction, the active char is then collected in the cold container. The mass of char and water trapped into bottles was measured to achieve the mass balance.

Finally, the matter and energy balance of each process was carried out by exploiting the collected results, then, a global one was established.

It should be noted that preliminary tests were conducted before real activation experiments:

- ❖ A first one which consists of a pyrolysis test without activation step in order to carry out the energy and matter balance of the pyrolysis step.
- ❖ A second to determine the duration of the activation step according to the wanted burn-off. This second test consists in a total activation of the pyrolysis char. Using the evolution of the gas produced during total activation step, burn-off could be calculated as a function of the reaction duration.

These two-test types have been doubled to evaluate reproducibility. The gap between two tests whatever the type of test was lower than 3 % for all measurements (mass of char and gas produced).

During total activation test, measurements of gas tar content has been done using a methodology adapted from tar protocol [21] and described in detail in [22].

3.3 Produced materials characterization

3.3.1 Ultimate analysis

The element analysis of the biomass, pyrolyzed material, and activated carbons was realized in a Thermofinnigan Flash EA 1112 Analyzer in order to determine carbon, hydrogen, nitrogen and oxygen contents.

3.3.2 Proximate analysis

The volatile, the carbon fix and the ash rate of the biomass (DPS), char (DPSC), and activated carbons (DPSAC) were determined by the thermogravimetric analysis. This analysis was performed on a Thermobalance (NETZSCH STA 449 F3 Jupiter). A small material mass is needed to carry out the analysis. About 30 to 50 mg was placed in the crucible, and a flow of argon (30 mL/min) was swept for 20 min before that, the heating program was launched in order to have an inert atmosphere. The experiment was realized as following:

- Dried the material at 378K in oven for 48h.
- Placed 30 to 50 mg in the crucible.
- Make the atmosphere inert.
- Increased the temperature from room temperature to 1073K under argon flow.
- Keep the experiment in this temperature for 60 min under inert atmosphere.
- Heated the material until attain the temperature of 1173K at rate of 40K/min under air flow.
- Keep the temperature during 30 min to allow pyrolysis char to be totally oxidized under air.

The NF EN 14775 standard was applied to determine the ash rate of DPS. 300 g of dried DPS was burned in a muffle furnace at 823K during 24h, the residual material was weighed.

3.3.3 Calorimetry analysis

The high heating value HHV (KJ/Kg) of the examined materials was performed using a bomb of calorimeter (Parr 6100, USA) according to ASTM D5865-07 method (ASTM International, 2013). About 300 mg of

sample was introduced in a capsule which was contacted with an ignition source using a platinum wire. Then, the whole was placed in the combustion vessel. In order to create the needed conditions of the combustion reaction, the oxygen at 20 bar was injected in the vessel. After that, the vessel was plunged in a bucket of deionized water. The result of the difference in temperature before and after combustion reaction was used to determine the samples' HHV. Furthermore, the low heating value LHV (KJ/Kg) was deduced using the determined value of %H by ultimate analysis following this relation:

$$LHV = HHV - 226. \%H \quad (1)$$

3.4 Energy and matter balance calculation method

The calculations of the obtained parameters which were collected from the pyrolysis and activation processes such as gases compositions and production, energy and matter balances were described in detail in [23]. The assumptions that used to accomplish these calculations were also exposed in the cited paper.

4 Results

4.1 Proximate analysis

The determined results of proximate analysis i.e. the values of volatiles compound, fixed carbon and rate of ashes of the biomass, pyrolyzed material and gasified materials are illustrated in Table 1. As can be observed, these results are similar to the literature.

Table 1: Proximate analysis of spikelet date palm materials.

	Volatiles	Fixed carbon	Ashes
DPS	83.1	15.8	1.1
DPSC-1	19.9	71.6	8.5
DPSC-2	19	70.5	10.5
DPSAC60-1 (*)	30	48.8	21.2
DPSAC60-2 (*)	22.1	60.6	17.3
DPSAC70-1 (*)	28.3	47.6	24.1
DPSAC70-2 (*)	17.7	62.3	20
DPSAC80-1 (*)	20	60	20
DPSAC80-2 (*)	22	56	22

(*) 1 and 2 represent the 1st and 2nd test.

Results obtained are quite logical. Concerning pyrolyzed biomass (DPSC), results are homogeneous and show an increase in the ash content induced by the loss of organic matter during pyrolysis step, inorganic material being more stable (not volatilized) and therefore condensed in the char. By the same way, the volatile matter content decrease significantly (removal of Oxygen and Hydrogen) to the profit of carbon fix rate during pyrolysis which is a classical trend.

Concerning activated chars (DPSAC...), results are less homogeneous but stay logical. An increase of the ash content is observed which is due to volatilization of carbon during activation step, implying also a decrease in the carbon fix content. These results are also confirmed by heating values measurement which decreases in activated chars since combustible material (mainly carbon) is diluted in mineral content during activation process.

4.2 Low and high heating values

The higher heating values (HHV) and lower heating values (LHV) obtained from measurements are presented in Table 2. The raw biomass sample (DPS) exhibited HHV and LHV values of approximately 17000 and 16000 KJ/Kg, respectively, serving as a reference for assessing the effects of pyrolysis and subsequent activation processes. These values are quite lower than those of wood mainly because of a higher mineral content. Following pyrolysis at 850 °C (1123 K), a significant increase in both HHV and LHV was observed, reaching values exceeding 24000 and 23000 KJ/Kg, respectively. This enhancement is attributed to the elevated carbon content in the char and the concurrent reduction in hydrogen and oxygen content during thermal decomposition.

Conversely, the activation of the char leads to a progressive decline in HHV and LHV as the burn-off rate increases from 60% to 80%. The HHV and LHV values decreased from approximately 24000 and 23000 KJ/Kg to around 12000 KJ/Kg. This reduction is due to the reaction of the char with water molecules during the activation process, which reduces the carbon content to the profit of mineral content. The combustible is therefore diluted in mineral compounds justifying the observed trend. Table 2: HHV and LHV values of the date spikelet materials.

Table 2 : Low and high heating values of the produced materials.

	HHV (kJ/kg)	LHV (kJ/kg)
DPS	17392	16036
DPSC1	24074	23802
DPSC2	28491	28220
DPSAC60-1	16195	15969
DPSAC60-2	19141	18915
DPSAC70-1	16478	16252
DPSAC70-2	16495	16269
DPSAC80-1	12392	12166
DPSAC80-2	12224	11998

4.3 Matter balance of pyrolysis step

4.3.1 Pyrolysis matter balance

It has to be noticed that the mass of condensable collected in the gas cleaning system did not allow to obtain a good matter balance since the gas cleaning system was not enough efficient to collect all the condensable. It has therefore been decided to estimate the mass of condensable through this calculation method:

$$Mass_{Condensables} = Mass_{DPS} - Mass_{DPSC} - Mass_{pyrolysis\ gases} \quad (2)$$

Figure 4 represents the matter balance of the pyrolysis phase of date palm spikelet DPS at 1123K. The mass balance (in mass percentage), shown in the Figure, details the amounts of char, gases, water, and tars produced from 100 g of biomass. This step aims to determine the outputs yields of the by-products after thermochemical treatment of date palm spikelet to supply technical information indispensable to elaborate a techno-economic study of such a process.

The distribution of by-product pyrolysis shows that the condensable (tars and water) constitute about 40% of the balance with dominance of tars (%Tars = 30.4%). The condensable came from the condensation of the procedure during the pyrolysis process. This result could be due to the fact that the water content within the biomass significantly influences the quantity and composition of condensable gases. M Jesus et al. [24] found similar result obtained from the pyrolysis of *Eucalyptus* wood with a rate of tar superior to 40%. The gases (non-condensable gases) that generated represent 30.3%, and the char (pyrolysis solid product) constitutes around 28.3% of the balance. The results of the rate of pyrolysis sub-products are in agreement with the literature and this behavior is recurrent in the biomass study under low pyrolysis conditions [25–27].

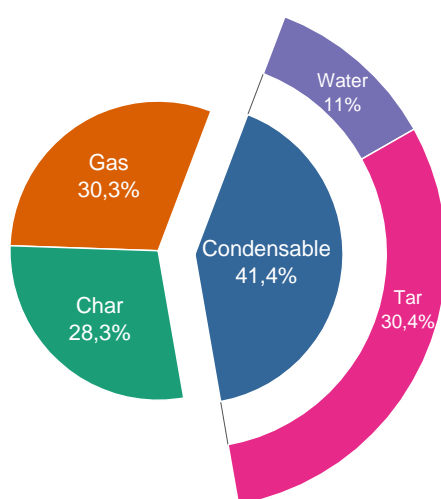


Figure 4 : Date palm spikelet (DPS) matter balance of the pyrolysis process.

4.3.2 Pyrolysis gas composition

The composition of generated gases during pyrolysis step was presented in Figure 5 while the production gases volume (NL/Kg) was illustrated in Table 3. The non-condensable gases collected from the pyrolysis process are H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄, and C₂H₆. As can be observed, H₂, CO and CO₂ were the major products with a cumulated proportion representing around 90 % (around 30 % for each component), followed by CH₄ with rate of 8%. Thus, a small proportion of C₂H₂, C₂H₄, and C₂H₆ is observed (≈1.4%). These results could be attributed to the depolymerization of date palm spikelet's structural compounds, primarily cellulose and lignin [28–30]. The observed range of gas production may also be assigned to the chemical transformation of cellulose, the main chemical constituent of date palm spikelet [31–34].

It was found that at temperatures below 600°C, very little H₂ is generated, with lignin being the primary compound responsible for its formation [35]. The production of CO and CO₂ could be attributed to the emission of C=O, C-O and C-C groups present in hemicelluloses, and in the linear polymer chain of cellulose. Additionally, the production of CO₂ could be assigned to the decarboxylation and depolymerization reactions that occur during the secondary reactions of volatile materials [31,36].

From Table 3, the total gas volume produced during pyrolysis process was 271.3 NL per 1 Kg of biomass. The H₂ and CO₂ occupied an important volume that is superior to 85 NL/Kg followed by CO with 73.5 NL/Kg.

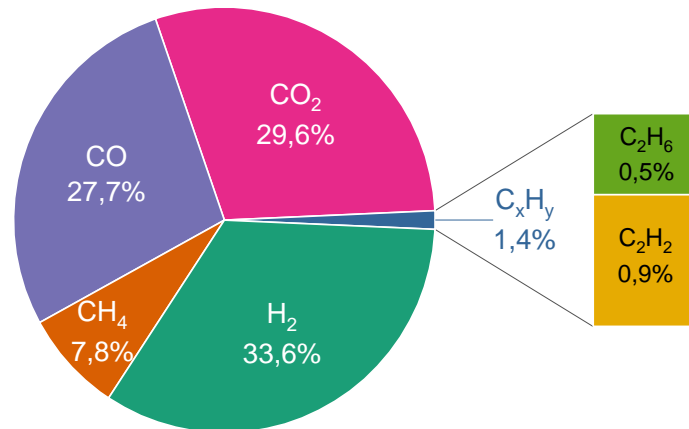


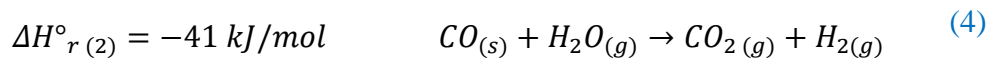
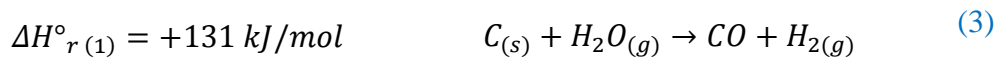
Figure 5 : Gases composition (Volumetric % on dry basis) of DPS pyrolysis at 1173 K and 10 K/min.

Table 3 : Gas production of each pyrolysis product in SL (Liter in standard conditions; 0°C; 1 bar) per kilogram of dry DPS.

Production gases volume (SL/kg dry DPS)								
	H ₂	CH ₄	CO	CO ₂	C ₂ H ₆	C ₂ H ₂	C ₂ H ₄	Total gas
Pyrolyzed biomass	86.4	21.6	73.5	85.8	1.4	2.5	0.1	271.3

4.3.3 Activation matter balance

The aim of this step is to evaluate the steam activation process through a matter balance activation study and to provide experimental data for a future techno-economic analysis. These results are considered as response to the activation of 100 g of chars produced as the output of the pyrolysis process. Table 4, regrouped different parameters input and output activation process. The activation process is mainly governed by two chemical reactions: a first one in heterogeneous phase between char and steam (consumption of solid carbon with water steam and development of char porosity: reaction (3)), and a second one in homogeneous phase between gases which converts carbon monoxide into carbon dioxide and hydrogen using water steam as a reagent. These two chemical reactions are detailed as following [37]:



As described in the pyrolysis matter balance part, the condensation system at the outlet of the reactor (gas cleaning system) was not efficient enough to trap all the condensable (remaining steam after activation reaction). Therefore, the input mass in the activation reaction considered is the sum of the pyrolysis char (DPSC) with the mass of water needed for activation. The mass of water needed being calculated knowing the number of moles of CO et CO₂ produced and according to reactions (3) and (4) [23].

From Table 4, the mass balance was found to be superior to 99% for all the activated carbons. These results show that the assumptions which were used to estimate the activation process are reliable. The increase of burn-off from 60 to 80% leads to an increase of the need in water and of the gas production with a decrease of the activated char quantity. All these results are logical since the increase in burn-off involves an increase of the degradation of the pyrolysis char. Consequently, this results in a decrease in the mass of the activated char, an increase of the quantity of produced gases and an increase in the need of water to assume carbon degradation through reaction (3) and carbon monoxide consumption through reaction (4).

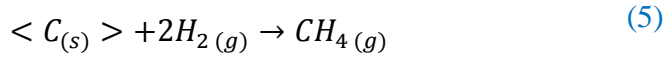
Table 4 : Date palm spikelet (DPS) matter balance of the activation process.

Activation Process of 100 g of char						
	m (g)					
	DPSAC60-1	DPSAC60-2	DPSAC70-1	DPSAC70-2	DPSAC80-1	DPSAC80-2
Char	100.0	100.0	100.0	100.0	100.0	100.0
Need water for activation	121.0	121.0	152.4	145.3	172.4	161.6
Total mass input	221.0	221.0	252.4	245.3	272.4	261.6
Produced activated carbon	38.5	40.4	24.7	28.7	18.2	18.0
Gas	180.9	178.6	220.2	210.9	249.0	242.4
Total mass output of	219.4	219.0	244.8	239.5	267.2	253.4

activation						
Balance (%)	99.3%	99.1%	97.0%	97.6%	98.1%	96.9%

4.3.4 Activation gas composition

The composition of generated gases during the gasification process is summarized in Table 5. According to these results, H₂, CO₂, and CO constitute more than 99% of produced gases. H₂ forms 53% to 60 % of this composition, followed by CO, then CO₂. The presence of CH₄ (≈0.2%) in this phase could be assigned to the methanization of the char by H₂ as reported by [38,39] via the following reaction:



Taking into account the three reactions considered (3), (4) and (5), it is theoretically possible to evaluate the H₂ gas composition using the following equation:

$$\%H_2 = \%CO + 2\% \times CO_2 - 2\% \times CH_4 \quad (6)$$

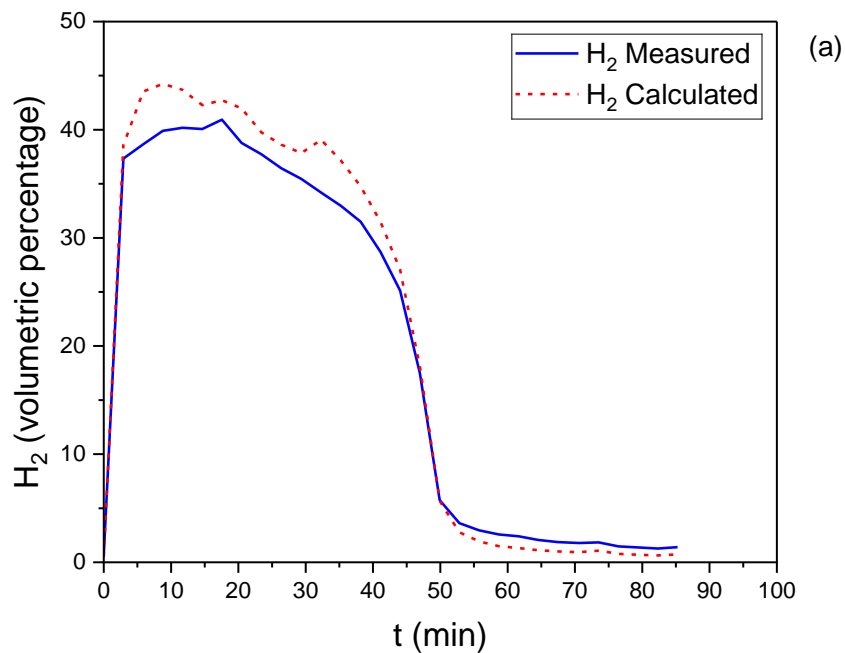


Figure 6 : H₂% activation yield – measured vs. predicted values.

As it can be seen on the Figure 6, there is a good fitting between calculated and measured values of H₂ volumetric percentage in produced gases showing the accuracy of the proposed reaction mechanism (i.e. Reaction (3), (4) and (5)).

It has to be noticed that the gas composition is toughly dependent on the residence time of gases in the hot zone, namely for reaction (4), in homogeneous phase. It means that, for a reduced residence time, extent of reaction (4) will be reduced which will involve a lower production of hydrogen and carbon dioxide to the profit of carbon monoxide. In the same way, an increase of residence time will increase the extent of

reaction (4) and involve a higher hydrogen and carbon dioxide level to the detriment of carbon monoxide production. This last effect is nevertheless limited by thermodynamic equilibrium of reaction (4). Ming Z et al. [40] found that the high temperature optimizes the reactions (3) and (4) which can contribute to the production of H₂, CO₂, and CO, especially, the production of H₂.

Table 5 : Composition of activation produced gases.

Activation process gas composition							
%	H ₂ measured	CH ₄	CO	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
DPSAC60-1	57.9	0.3	24.8	17.0	0.01	0.01	<0.01
DPSAC60-2	60.1	0.2	23.1	16.5	0.01	0.01	<0.01
DPSAC70-1	53.2	0.2	25.4	21.2	0.01	0.01	<0.01
DPSAC70-2	58.2	0.2	22.7	18.9	0.01	0.01	<0.01
DPSAC80-1	57.0	0.1	24.7	18.2	0.01	0.01	<0.01
DPSAC80-2	55.6	0.3	25.6	18.5	0.01	0.01	<0.01

Considering the objective of H₂ production, a last step of separation needs to be considered. The reference technology for H₂ separation is the *pressure swing adsorption* (PSA) [8]. Other technologies exist such as *temperature swing adsorption* (TSA) [7] and membranes [6].

Considering PSA, Spath et al [8] stated that a hydrogen concentration of minimum 70 % has to be reached before entrance in PSA step to obtain a good H₂ purity (99.9%) needed for next application, such as production of electricity in a fuel cell [41].

In the work of Demol et al [4], H₂ separation unit is based on both membrane and PSA technologies since H₂ content is not enough at the outlet of the gasification system to be used only in a PSA system. In our case, it is important to highlight the fact that, H₂ content, without any optimization, is ever about 60 %. This value could reach the limit of 70% just by increasing the residence time of gases in the activation reactor to promote reaction (4). Only a PSA system could therefore be used for H₂ separation with an efficiency of extraction of about 85 % [8].

4.3.5 Global matter balance

The global matter balance represents the process from dried raw material and the pyrolysis by-products to the activation by-products. Table 6 regrouped all these results, starting with 100 g of dry Palm spikelet. As can be seen, 100 g of biomass could produce 28.7 g of pyrolysis char, 28.8 g of dry pyrolysis gas, and 42.5 g of condensable. Then, the mass of the activated carbon decreases with the increase of burn-off – around 11.8 and 5 g for DPSA60, DPSA70 and DPSA80, respectively - while the mass of produced gas augments. This last result is logical since increase in burn-off involves a higher level of degradation of char to the profit of the gas production. The value of $\Delta w\%_{\text{Activation}}$ is around 2-3% which indicates that the measurements methodology and results presented are accurate. To clarify Table 6, a Sankey diagram is shown in Figure 7 :

Sankey diagram of global matter balance process (case of DPSAC60-1) starting from dry DPS. [Figure 7](#) with DPSAC60-1 serving as a representative example.

Table 6 : Global matter balance of pyrolysis – activation processes (g or wt%)

Biomass	DPS					
Dry biomass (Total mass input)	100					
Produced char	28.7					
Produced gas	71.3					
- Dry gas	28.8					
- Condensable	42.5					
- Water	11.0					
- Tars	31.5					
Pyrolysis products (Total mass output)	100.0					
$\Delta w\%$ (pyrolysis)	0					
	DPSAC60-1	DPSAC60-2	DPSAC70-1	DPSAC70-2	DPSAC80-1	DPSAC80-2
Char	28.7	28.7	28.7	28.7	28.7	28.7
Needed water for activation	31.6	30.7	40.9	38.5	43.9	43.8
Total mass input	60.3	59.5	69.7	67.2	72.6	72.5
Produced activated carbon	11.1	11.6	7.1	8.2	5.2	5.1
Produced gas	46.7	45.6	58.8	56.2	64.2	64.0
- H ₂	3.5	3.7	3.6	4.1	4.6	4.3
- CO	20.7	19.7	23.8	22.5	27.6	27.9
- CO ₂	22.3	22.1	31.3	29.4	31.9	31.6
- CH ₄	0.1	0.1	0.1	0.1	0.1	0.2
Total mass output	57.7	57.2	65.9	64.4	69.4	69.1
$\Delta w\%$ (activation)	2.6	2.3	3.7	2.9	3.2	3.4

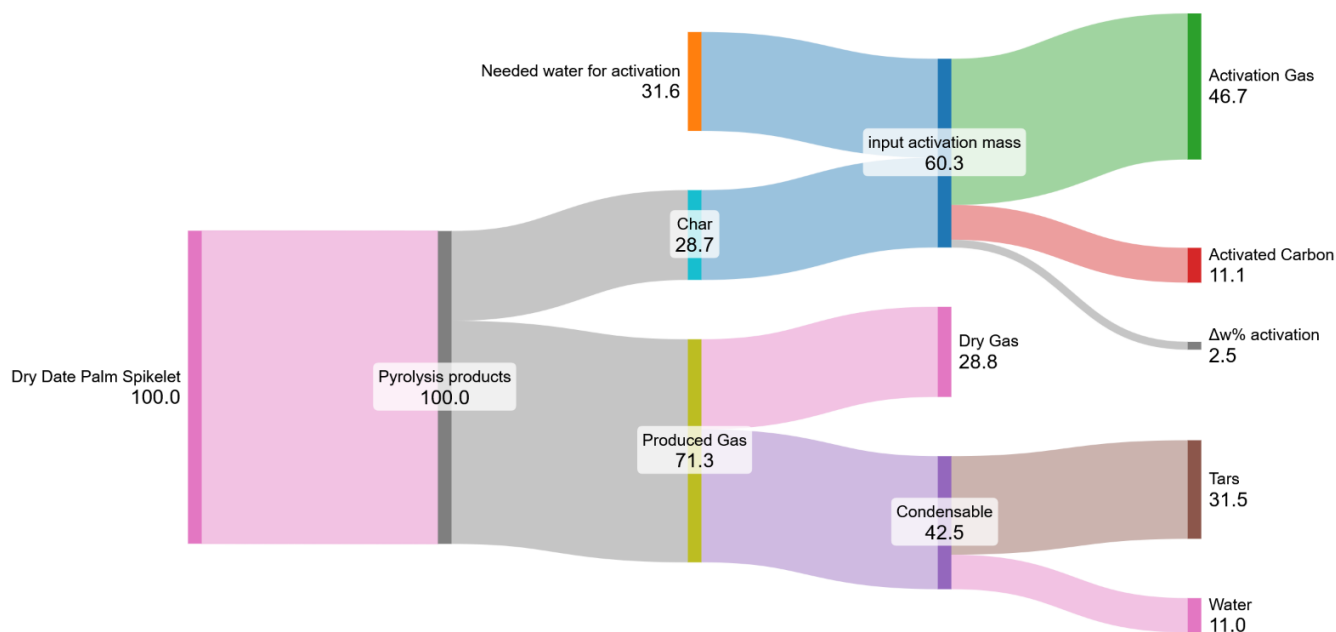


Figure 7 : Sankey diagram of global matter balance process (case of DPSAC60-1) starting from dry DPS.

4.3.5.1 Gas and hydrogen production

Considering gas production, between 45% and 64% of the initial weight of dry biomass is converted into gases during activation process. It has to be noticed that tar content has been evaluated in activation gases during preliminary total activation tests. Values of tar content was considerably lower than those reported in literature for gas produced from biomass gasification [42]. Indeed, benzene, toluene and naphthalene content were respectively around 300, 10 and 3 mg/sm³. For heavier PAH, values were lower than detection limits (0.5 mg/sm³). The really high quality of the activation gases highlights the fact that their valorization only under heat form is not the best option. Indeed, many studies focus on hydrogen or syngas (synthetic methane) production from biomass through gasification process [42]. It is therefore interesting to compare the hydrogen production obtained in this work to values reached in gasification processes.

According to burn-off value, hydrogen production reaches between 35 to 46 g/kg which represents a good production according to literature. Demol et al. [4] reports theoretical hydrogen production of 107 and 47 g/kg using bubbling fluidized bed technology under conditions of oxy/steam gasification and for two different scenarios. In the first scenario where the higher hydrogen production is reached, a lot of devices are used to improve hydrogen production (water gas shift reactor. steam reformer) making the process really complex. In the second scenario, this device has not been used, and the hydrogen production is slightly higher than in this study but with a more complex process. Other references deal with hydrogen production but values are given after the hydrogen separation process which is mainly done using PSA (Pressure swing adsorption system) and which allows to reach around 75 % of H₂ separation efficiency [4]. Using this value of H₂ separation efficiency, quantities of hydrogen recoverable from the activation process detailed in this article could be in the range of 26 to 35 g/kg. In comparison. values of 76.1. 75.2. 107.4 are reported respectively by Ersöz et al [43], Pallozzi et al [44] and Gupta and Dasappa [45]. These really high hydrogen

productions presented in literature are extracted from theoretical works through numerical simulation which does not take into account potential technical problems such as degradation of separation method efficiency caused by tar content in gas.

The low tar content of activation gases could assume a largely slower degradation of H₂ separation apparatus and make therefore this way of hydrogen production more realist.

4.3.5.2 Water demand

It appears that the steam need for activation process represents a high quantity of water – between 31 to 44% of initial dry biomass weight – which increases the impact of such a process on environment. Nevertheless, it could be noticed that water needed for activation process could take his source partially in steam produced during drying stage of biomass (not studied in this article) according to initial moisture content in the raw biomass. This point could therefore be optimized.

Taking into account initial moisture content on DPS when harvested (around 25%) and making the assumption that steam produced during the drying step could be used to supply activation process, the global matter balance could be recalculated. The new global matter balance after optimization is then presented under a Sankey diagram form on figure 8. After optimization of the process, the extra demand in water only represents 6.6 % of the initial dry mass of biomass burn-off of 60 % (case of DPSAC60-1) which is drastically lower than 31.6 % without optimization. This value reaches around 19% for DPSAC80-1 (instead of 44% without optimization).

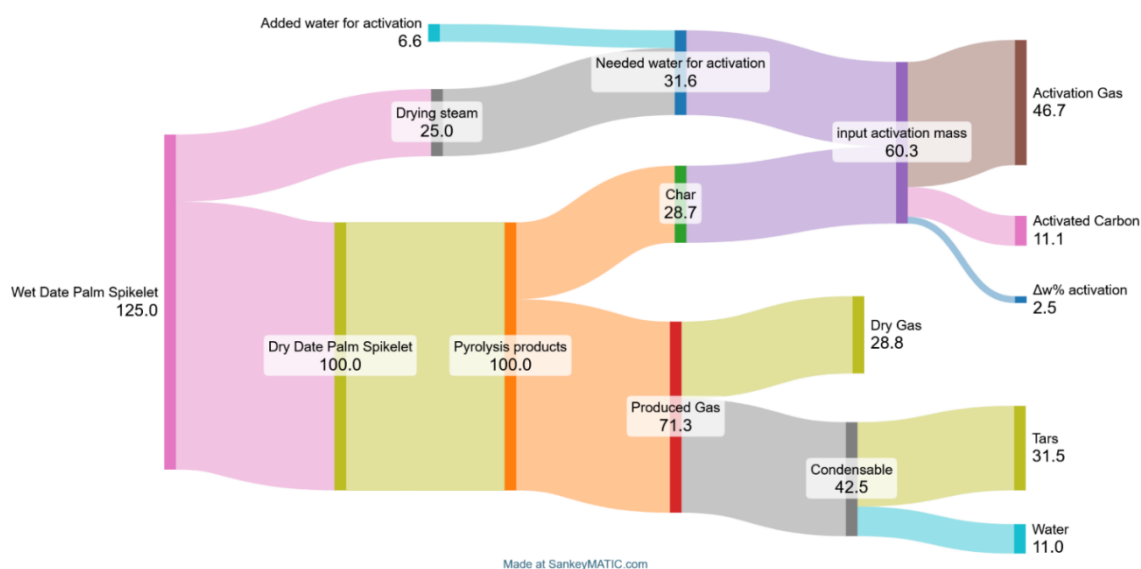


Figure 8 : Sankey diagram of global matter balance process (case of DPSAC60-1) starting from wet DPS.

4.4 Energy balance

4.4.1 Pyrolysis energy balance

The energy balance of the pyrolysis step was carried out using the pyrolysis data of the calorimetry analysis of solid materials and the balance matter pyrolysis. Table 7 summarized both energetic parameters i.e. energy and proportion for input and output pyrolysis process. The energy input of the process is assumed to

be the sum of the energy contained in the dry biomass added to the energy needed to heat it from room temperature to 1123K, assuming that pyrolysis process is athermal between 273 and 1173K [42]. The energy needed for drying the biomass is not taken into account in this work.

Regarding the energy output, it represents the sum of energies contained in produced gases, char, and condensable. Knowing that energy contained in condensable (not measured) has been calculated assuming a complete energy balance of the pyrolysis process, it is therefore logical to find the same value between total input and output energy for this step. Assuming that all gases (dry + condensable) will be burned to supply energy for the pyrolysis step. The energy recoverable from the last one is equal to total output energy minus energy needed for the process. The results indicate that around 50 % of the energy input of the process (\approx 53.4 % of the energy initially contained in dry DPS) could be recovered from pyrolysis gases.

As can be observed, more than 93% of input energy is concentrated in the biomass and the process input forms just around 6% of the demanded input energy. Furthermore, the proportion of energy contained in pyrolysis gases was 56.4% and that of the produced char was 43.6%. This could be assigned to the transference of energy from char to the generated gases (condensable and non-condensable). Z Wong et al. [46] found that at high pyrolysis temperature the proportion of energy in the pyrolysis gases augments and this behavior could be attributed to the LVH of the dried biomass.

Table 7 : Energy balance of the pyrolysis process (KJ for 100 g of dry biomass and in % of total energy input).

		kJ (for 100 g of dry input DPS)	Energy % compare to total input energy (dry biomass + pyrolysis process)
		DPS	
Energy input	Dry Biomass	1604	93.6
	Process	110	6.4
	Total energy input	1713	100.0
Energy output	Char	748	43.6
	Dry gas	292	17.1
	Condensable	673	39.3
	Pyrolysis Gases	966	56.4
	Total energy output	1713	100.0
Energy recoverable from the pyrolysis process (pyrolysis gases - process)		856	49.9

4.4.2 Activation energy balance

The energy balance of the gasification process of the produced char from pyrolysis phase was calculated for different burn-off value of fabricated activated carbons i.e. 60. 70 and 80%. Results that were shown in Table 8 represent the obtained data energy in KJ per 100 g of pyrolyzed char. The distribution of energy (%)

according to the total input mass is also given knowing that total energy input is assumed to be the sum of the energy contained in pyrolysis char, the energy needed for gasification reactions ((3) and (4) and the one for steam production. First of all, it appears that the energy balance of the activation process obtained by comparison of total energy output (activated char + activation gases) to energy input without taking account the energy needed for steam production is between 95 % to 106 % for all tests apart for DPSAC70-1 which is lower than 90 %. It shows the accuracy of measurements and of the reliability of experimental data collected here.

4.4.2.1 Energy need for steam production

Taking into account the energy needed to produce steam, the energy balance falls by around 15 %. The heat need for steam has been calculated taking into account the heating of water from 293K to 373K, vaporizing of water into steam and heating the steam flow from 293K to 1123K. As discussed in global matter balance part, in an industrial plant, steam produced during biomass drying could be used to supply activation step meaning that energy demand is only the one needed to heat the steam from 293K to 1123K, only representing 35 % of the previous one. The remaining 65% corresponding to water heating and vaporization which represents heat required for biomass drying. It means that, with assumptions taken into account for energy balance calculation, energy demand of pyrolysis step is underestimated and the one for activation is over evaluated. Nevertheless, it won't have any impact on the global energy balance detailed later. Moreover, the activation gases at the outlet of the activation step are at high temperature and contains residual steam. These gases have to be cooled down to condensate steam before valorization step of activation gases. Then, it is possible to use steam produced in the drying step to cool down activation gases – through a heat exchanger, involving a heating of drying steam used after as activation agent. This last option could be useful to improve significantly the global energy efficiency of the process. It will be taken into account in the global energy balance presented in the next part of the article (4.4.3).

4.4.2.2 Gas and hydrogen energy content

As can be seen, H₂ contained energy is the major if compared with CO and CH₄ and formed between 40 to 53% with the increase of burn-off from 60% to 80% of the energy input in activation process corresponding also to 55 to 73 % of pyrolysis char energy.

This result is in agreement with the matter balance of gasification process. Moreover, the total gases energy represents 63 to 83 % of the energy input in activation process corresponding also to 86 to 110 % of pyrolysis char energy. The fact that total gas energy could reach a higher value than those of initial pyrolysis char is due to the fact that energy needed for activation reaction ((3) and (4)) is not taken into account in the last calculation.

The increase of the energy contained in gases with burn-off is mainly due to increase of gas production detailed in matter balance and in agreement with literature [47]. The LHV of activation gases is quite constant and about 9.5 MJ/sm³.

The same behavior was noted for the energy input process i.e. the needed energy to the gasification (reactions (3) and (4)) and to produce steam.

The energy content of activation gases presented in this part is calculated taking into account only LHV of each compound, sensible heat of gases not being considered. As it has been discussed in part 4.4.2.1), activation gas stream at the outlet of the activation reactor is at high temperature (1173K) and has to be cooled down before the valorization of activation gases. This extra energy could then be used to supply the process for the drying steam heat before activation step.

Table 8 : Energy balance of the gasification process (KJ/Kg or %E).

		DPSAC60-1		DPSAC60-2		DPSAC70-1		DPSAC70-2		DPSAC80-1		DPSAC80-2	
		E (kJ) ¹	%E ²	E (kJ) ¹	%E ²	E (kJ) ¹	%E ²	E (kJ) ¹	%E ²	E (kJ) ¹	%E ²	E (kJ) ¹	%E ²
E input in process (kJ)	Initial char	2617	72.5	2617	72.5	2617	72.5	2617	72.5	2617	72.5	2617	72.5
	Activation reactions ((3) and (4))	501	13.9	481	13.3	616	17.1	580	16.1	682	18.9	684	18.9
	Steam production ³	491	13.6	477	13.2	636	17.6	598	16.6	682	18.9	679	18.8
	Total input	3609	100.0	3576	99.1	3868	107.2	3796	105.2	3981	110.3	3980	110.3
E output from process (kJ)	Activated carbon	691	19.1	725	20.1	379	10.5	441	12.2	539	14.9	566	15.7
	Generated gases	2259	62.6	2304	63.9	2425	67.2	2604	72.2	2979	82.5	2903	80.5
	H ₂	1448	40.1	1533	42.5	1496	41.5	1725	47.8	1913	53.0	1811	50.2
	CO	790	21.9	750	20.8	908	25.2	856	23.7	1052	29.2	1061	29.4
	CH ₄	21	0.6	19	0.5	21	0.6	20	0.6	13	0.4	31	0.9
	Total Output	2950	81.7	3029	83.9	2805	77.7	3044	84.4	3518	97.5	3469	96.1
E recoverable from activation process (kJ)		1267	35.1	1346	37.6	1174	30.4	1426	37.6	1615	40.6	1540	38.7
Energy balance (%)	Energy Balance (without energy needed for steam generation)	94.6		97.7		86.8		95.2		106.6		105.1	
	Energy Balance (with energy for steam generation)	81.7		84.7		72.5		80.2		88.4		87.1	

¹Energy for activation of 100 g of pyrolysis char

²Energy distribution according to total energy input of the activation process

³Energy for steam production = energy to heat water from 293 K to 373 K, to vaporize water and to heat the steam from 373K to 1173K

4.4.3 Global energy balance

As for global matter balance, it has been decided to present global energy balance by adding a first step of drying making the following assumptions related to previous discussions:

- ❖ Initial biomass moisture content is fixed at 25 % involving necessity of a drying step;
- ❖ The energy needed for steam production given for activation step in table 8 is divided in 2 parts:
 - The energy needed for water heating (from 293K to 373K) and vaporization is attributed to biomass drying step;
 - The energy needed for steam heating (373K to 1123K) is attributed to steam heating step;
- ❖ The energy collected during the cooling of activation gases (sensible heat) from 1173K to 293K has been added to the energy balance;
- ❖ The energy needed for activation step (both for activation reactions ((3) and (4)) and for steam heating) is collected from heat produced by burning pyrolysis gases;
- ❖ The extra heat not used (from burning of pyrolysis gases and from cooling of activation ones) is send to an external heating network;
- ❖ The activation gases are conserved for a potential valorization (i.e. hydrogen. syngas or methanol production).

The global energy balance of the pyrolysis – gasification process starting from the wet biomass i.e. date palm spikelet until activated carbon and generated gases is depicted in [Table 9](#). To simplify the analysis of the data and make it useful, these results express the generated energy (in KJ or %) from the thermochemical treatment of 1 Kg of dry raw material (DPS) using steam.

These results are also presented on [Figure 9](#) as a form of a Sankey diagram for a better comprehension:

Table 9 : Global energy balance of pyrolysis – activation processes (kJ or %E).

		E (kJ) ¹						%E ²						
Drying process	Energy input	Wet biomass	15124						94.3					
		Drying process ³	912						5.7					
	Energy Output	Dry biomass	16036						100.0					
Pyrolysis process	Energy Input	Dry Biomass	16036						100.0					
		Process	1099						6.9					
	Energy Output	Char	7478						46.6					
		Dried gas	2924						18.2					
		Condensable	6733						42.0					
		Pyrolysis gases (dried gas + condensable)	9657						60.2					
Total (Pyrolysis gases + Char)		17134						106.9						
Activation Process			E (kJ) ¹	%E ²	E (kJ) ¹	%E ²	E(kJ) ¹	%E ²	E (kJ) ¹	%E ²	E (kJ) ¹	%E ²	E (kJ) ¹	%E ²
			DPSAC60-1		DPSAC60-2		DPSAC70-1		DPSAC70-2		DPSAC80-1		DPSAC80-2	
	Energy Input	Char	7478	46.6	7478	46.6	7478	46.6	7478	46.6	7478	46.6	7478	46.6
		Activation reactions ((3) and (4))	1430	8.9	1376	8.6	1759	11.0	1657	10.3	1950	12.2	1954	12.2
		To heat steam ⁴	491	3.1	477	3.0	636	4.0	598	3.7	682	4.3	679	4.2
		Total input	9399	58.6	9331	58.2	9872	61.6	9733	60.7	10109	63.0	10111	63.1
	Energy Output	Activated Carbon	1973	12.3	2070	12.9	1084	6.8	1259	7.8	729	4.5	717	4.5
		Generated Gases (LHV)	6454	40.2	6584	41.1	6930	43.2	7440	46.4	8511	53.1	8295	51.7
		H ₂	4137	25.8	4381	27.3	4275	26.7	4930	30.7	5467	34.1	5175	32.3
		CO	2257	14.1	2142	13.4	2594	16.2	2447	15.3	3006	18.7	3031	18.9
		CH ₄	60	0.4	55	0.3	61	0.4	58	0.4	38	0.2	89	0.6
		Generated Gases (Sensible heat)	821	5.1	834	5.2	945	5.9	983	6.1	1106	6.9	1078	6.7
	Total Output		9248	57.7	9488	59.2	8959	55.9	9681	60.4	10346	64.5	10090	62.9
	Delta energy activation		151	0.9	-157	-1.0	913	5.7	52	0.3	-237	-1.5	21	0.1
Global process	Energy recoverable under heat supply to heating network ⁵		6546	40.8	6627	41.3	6197	38.6	6373	39.7	6121	38.2	6092	38.0
	Energy recoverable from the overall process ⁶		13000	81.1	13211	82.4	13127	81.9	13813	86.1	14632	91.2	14387	89.7
	Global efficiency ⁷		93.4		95.3		88.6		94.0		95.8		94.2	

¹Energy for activation of 1kg of dry biomass; ²Energy distribution according to energy in 1 kg of dry biomass (LHV); ³Energy for water heating and vaporizing; ⁴To heat steam from 373K (temperature of steam at the outlet of the drier) to 1173K (temperature needed for steam at inlet of the activation reactor); ⁵Energy contained in total pyrolysis gases - energies for different steps of the process (drying + pyrolysis process + activation steam heating + activation reactions) + energy collected during the cooling of activation gases; ⁶Heat (to heating network) + LHV of activation gases; ⁷Energy recoverable from the overall process + energy in activated char.

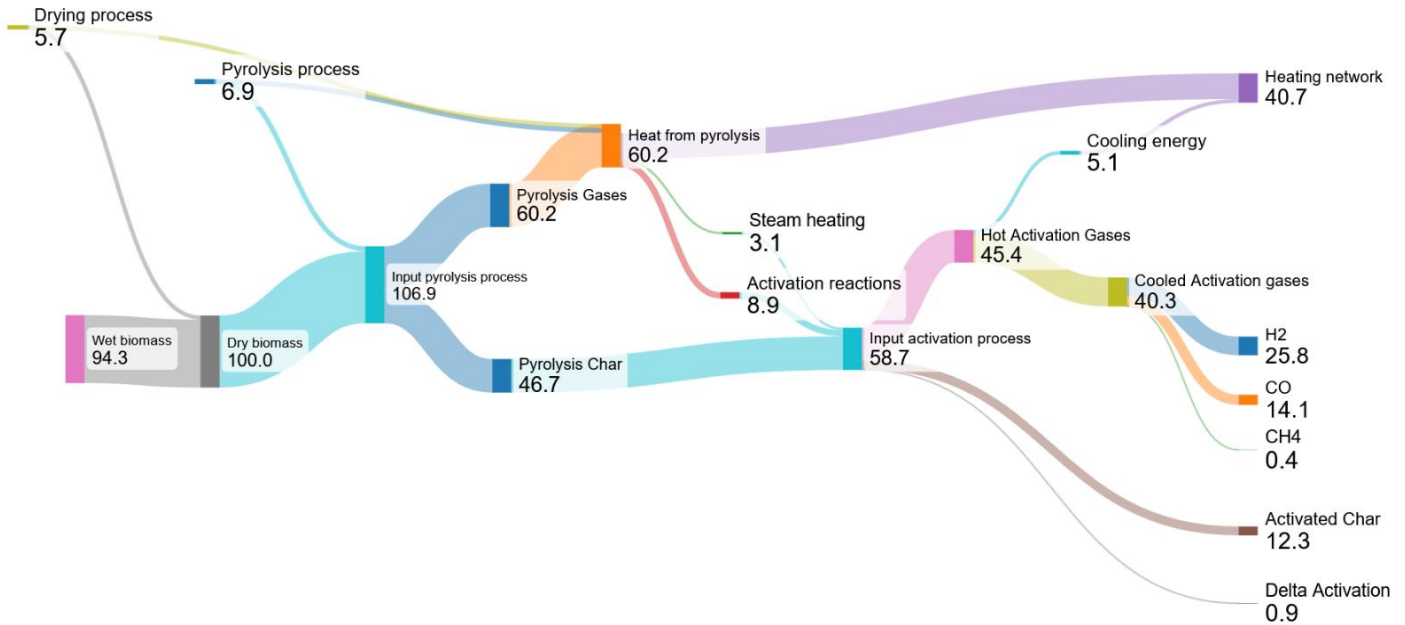


Figure 9 : Sankey diagram of global energy balance process (case of DPSAC60-1).

The interesting information which could be collected from the results presented in Table 9 are as follows:

- ❖ The heat which could be collected and supplied to a heating network represents between 38 to 41 % of the energy contained in dry biomass based on LHV;
- ❖ The heat contained in total activation gases (based on LHV of gas) is in the range of 40 to 53 % of the energy contained in dry biomass based on LHV;
- ❖ The sum of these two last values represents the energy recoverable from the overall process which is in the range of 81 to 91 %;
- ❖ By adding to this last value, the energy contained in the activated char, the thermal efficiency of the global process could then be evaluated between 93 to 96% excepted for DPSAC70-1 which is around 89% (because a non-explained lower production of H₂). It has to be noticed that these values do not take into account the heat losses that would occur in the various reactors of a real industrial plant, or the electrical energy required to supply the different actuators (motors, compressors, etc....).

To highlights the interest of the proposed process of co-production of hydrogen and active char, a comparison of obtained results with data collected in literature is given in Table 10.

Table 10 : Comparative study of different pyrolysis / gasification processes.

		Hydrogen energy efficiency ¹	Hydrogen production ²	Heat energy efficiency ¹	Char energy efficiency ¹	Char production	Technologies	Type of Data	Global efficiency ¹
		%	g/kg biomass (dry basis)	%	%	g/kg			%
Corella (2008) [48]		75.3	119				Oxy/steam biomass gasification in fluidized bed reactor + steam reforming catalytic reactor + Co-shift reactor	Experimental	
Gupta and Dasappa (2018) [45]		68.0	107.4				Oxy-steam gasification in a downdraft gasifier (fixed bed) + Water gas shift reactor	Experimental + Simulation	
Spath et al (2005) [8]		49.8	78.7	23.8			Low-pressure indirectly-heated entrained flow gasifier + steam reforming catalytic reactor + Water gas shift reactor	Simulation	97
Ersöz et al (2018) [43]		48.2	76.1				Oxy/steam biomass gasification in fluidized bed reactor + steam reforming catalytic reactor + Water gas shift reactor	Simulation	93
Pallozzi et al (2016) [44]		47.6	75.2	Heat converted to electricity			Steam biomass gasification in a dual fluidized bed + catalytic filters candle + Water gas shift reactor	Simulation	60
Susmozas et al (2016) [49]		34.8	55	Heat converted to electricity			Steam biomass gasification in a dual fluidized bed + steam reforming catalytic reactor + Water gas shift reactor	Simulation	
Demol et al (2021) [4]	Case N°1	57.6	91	25.9			Oxy/steam biomass gasification in fluidized bed reactor + Partial oxidation reactor + steam reforming catalytic reactor + Water gas shift reactor	Simulation	81.2

	Case N°2	25.3	40	65			Oxy/steam biomass gasification in fluidized bed reactor + Partial oxidation reactor		83.8
	Case N°3	16.7	26.4	52.4	20.4	110	Pyrolysis reactor + Partial oxidation reactor		86.6
This article	Burn-off: 60%	22.6	30.2	41	12.6	113.3	Pyrolysis reactor + activation reactor (rotary kilns)	Experimental	94.3
	Burn-off: 70%	24.4	32.6	39.2	7.3	76.6			91.3
	Burn-off: 80%	28.2	37.7	38.1	4.5	51.8			95.0

¹ without taking into account energy consumption of the process (electricity) and based on LHV of the dry biomass;

² by taking into account an 85% of H₂ separation efficiency.

Regarding hydrogen production, the values detailed in literature are in the range of 26 to 120 g H₂/kg of dry biomass with an average value closer to 70 gH₂/kg which is 2 times higher than production measured experimentally in this work. It could be noticed that technologies used for reaching so high hydrogen production yields are really complex and involve the use of a lot of different reactors mainly for tar cracking (steam reforming catalytic reactor) and for promoting water gas shift reaction (i.e. reaction (4); water gas shift reactors). It could also be added that all these works are based on simulated processes.

The valorization of the remaining heat is discussed in some papers only [8] and [4] which exhibit heat efficiency in the range of 26 to 65 % in comparison with 38 to 41% obtained in this work.

Only one reference Demol et al [4] deals with coproduction of hydrogen and char (biochar but no active char) using a simulated process more simple (with few steps) than others. The hydrogen production is then 26 g H₂/kg of dry biomass which is slightly lower than those obtained in this study. The remaining heat available to supply a heating network is assumed to be 52 % of the energy contained in dry biomass (on LHV basis) compared to around 40% in this work. Finally, char production is 110 g/kg of dry biomass which is close to values obtained between 60 and 80% of burn-off. All these comparisons with case N°3 of Demol et al [4] highlights the interest of the co-production of hydrogen and active char process proposed in this paper. Regarding the economic availability of such a process, it has to be highlighted that the char produced in this work of Demol et al. [4] is a biochar whose characteristics are different and which therefore cannot be used as active char. This point has an important effect regarding the economic efficiency of processes. Indeed, biochar price (\approx 350 €/ton; [50]) is more than 5 times lower than the one of active char whose price is closer to 2500 €/ton [51] and could even reach 10000 €/ton [52] for pharmaceutical uses.

The interest of this study is to provide a support to the industrials how desired a techno-economic study in order to exploit this abundant raw material.

5 Conclusion

This study successfully examined the co-production of hydrogen and activated carbons from an abundant Algerian biomass (date palm spikelet) by performing a matter and energy balance using an experimental method. The pyrolysis/gasification process was carried out to quantify the generated gases, condensable, and activated carbon. This paper focused on the simultaneous production of hydrogen and activated carbon through a simple and robust process, providing detailed gas compositions and comprehensive analyses of input and output matter and energies.

From this process, approximately 30 to 38 g of hydrogen and 50 to 113 g of activated carbon could be produced per kilogram of dry precursor. Furthermore, the process could generate heat equivalent to 38% - 41% of the input biomass energy.

The very high quality of gasification gases (extremely low concentration in tars, and high hydrogen content) close to 60 vol%), without any complex and energy intensive steps of gas cleaning and upgrading, has to be highlighted. It is one of the results showed in this work which could the best demonstrate the real interest of the technology proposed here in comparison with other hydrogen production technologies from biomass.

Our study therefore demonstrates the feasibility of producing renewable hydrogen from biomass, accompanied by the production of adsorbent materials that can be employed in environmental applications.

6 Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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9 References

- [1] Pandey S, Erbaugh JT. Driving sustainable uptake: a systematic review of global literature on policies governing woody biomass for energy. *Discov Sustain* 2024; 5: 28 n.d.
- [2] Lević J, Pržulj N, Mandić D. Biomass as a renewable energy source. *ОДРЖИВИ РАЗВОЈ И УПРАВЉАЊЕ ПРИРОДНИМ РЕСУРСИМА РЕПУБЛИКЕ СРПСКЕ* 2023;6.
- [3] Gielen D, Taibi E, Miranda R. Hydrogen: A reviewable energy perspective: Report prepared for the 2nd hydrogen energy ministerial meeting in tokyo, japan 2019.
- [4] Demol R, Dufour A, Rogaume Y, Mauviel G. Production of purified H₂, heat, and biochar from wood: comparison between gasification and autothermal pyrolysis based on advanced process modeling. *Energy & Fuels* 2021;36:488–501.
- [5] Mauerhofer AM, Schmid JC, Benedikt F, Fuchs J, Müller S, Hofbauer H. Dual fluidized bed steam gasification: Change of product gas quality along the reactor height. *Energy* 2019;173:1256–72.
- [6] Yin H, Yip ACK. A review on the production and purification of biomass-derived hydrogen using emerging membrane technologies. *Catalysts* 2017;7:297.
- [7] Golmakani A, Fatemi S, Tamnanloo J. Investigating PSA, VSA, and TSA methods in SMR unit of refineries for hydrogen production with fuel cell specification. *Sep Purif Technol* 2017;176:73–91.
- [8] Spath P, Aden A, Eggeman T, Ringer M, Wallace B, Jechura J. Biomass to hydrogen production detailed design and economics utilizing the Battelle Columbus Laboratory indirectly-heated gasifier. National Renewable Energy Lab.(NREL), Golden, CO (United States); 2005.
- [9] Demol R. Production d'hydrogène issu de gazéification de biomasse: modélisation, analyse technico-

- [10] Alharbi HA, Hameed BH, Alotaibi KD, Al-Oud SS, Al-Modaihsh AS. Recent methods in the production of activated carbon from date palm residues for the adsorption of textile dyes: A review. *Front Environ Sci* 2022;10. <https://doi.org/10.3389/fenvs.2022.996953>.
- [11] Bastidas-Oyanedel J-R, Fang C, Almardeai S, Javid U, Yousuf A, Schmidt JE. Waste biorefinery in arid/semi-arid regions. *Bioresour Technol* 2016;215:21–8.
- [12] Haghbin MR, Niknam Shahrak M. Process conditions optimization for the fabrication of highly porous activated carbon from date palm bark wastes for removing pollutants from water. *Powder Technol* 2021;377:890–9. <https://doi.org/https://doi.org/10.1016/j.powtec.2020.09.051>.
- [13] Al Malki M, Yaser AZ, Hamzah MAAM, Zaini MAA, Latif NA, Hasmoni SH, et al. Date palm biochar and date palm activated carbon as green adsorbent—synthesis and application. *Curr Pollut Reports* 2023;9:374–90.
- [14] Alharbi HA, Hameed BH, Alotaibi KD, Al-Oud SS, Al-Modaihsh AS. Conversion of a mixture of date palm wastes to mesoporous activated carbon for efficient dye adsorption. *Mater Res Express* 2023;10:15602.
- [15] Shoaib M, Al-Swaidan HM. Optimization and characterization of sliced activated carbon prepared from date palm tree fronds by physical activation. *Biomass and Bioenergy* 2015;73:124–34.
- [16] Khadhri N, El Khames Saad M, Ben Mosbah M, Moussaoui Y. Batch and continuous column adsorption of indigo carmine onto activated carbon derived from date palm petiole. *J Environ Chem Eng* 2019;7. <https://doi.org/10.1016/j.jece.2018.11.020>.
- [17] Islam MA, Tan IAW, Benhouria A, Asif M, Hameed BH. Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation. *Chem Eng J* 2015;270:187–95.
- [18] Rambabu K, AlYammahi J, Bharath G, Thanigaivelan A, Sivarajasekar N, Banat F. Nano-activated carbon derived from date palm coir waste for efficient sequestration of noxious 2, 4-dichlorophenoxyacetic acid herbicide. *Chemosphere* 2021;282:131103.
- [19] Daoud M, Benturki O, Kecira Z, Fontana S, Rogaume Y, Girods P. The effect of steam on the physicochemical properties of activated carbons based on Ziziphus jujube stones for reactive dye removal. *Biomass Convers Biorefinery* 2024;14:9557–70.
- [20] Daoud M, Kecira Z, Benturki O, Girods P, Rogaume Y, Fontana S. Characterization of novel adsorbents from Phoenix dactylifera rachis. Box–Behnken design, kinetic, and isotherm models for BEZAKTIV Red S-MAX dye adsorption onto the produced carbons. *Biomass Convers Biorefinery* 2023:1–19.
- [21] Simell P, Ståhlberg P, Kurkela E, Albrecht J, Deutsch S, Sjöström K. Provisional protocol for the sampling and analysis of tar and particulates in the gas from large-scale biomass gasifiers. Version 1998. *Biomass and Bioenergy* 2000;18:19–38.
- [22] Badu P, DEBAL M, Girods P, AUBERT S, ROGAUME Y. Biomass Gasification in an Autothermal Semi-Industrial Fluidized Bed Gasifier: Syngas Characterization and Energy Balance. Available SSRN 5013850 n.d.
- [23] Daoud M, Benturki O, Fontana S, Rogaume Y, Girods P. Energy and matter balance of process of activated carbon production from Algerian agricultural wastes: Date palm rachis and jujube stones. *Biomass Convers Biorefinery* 2021;11:1537–54.
- [24] Jesus MS, Napoli A, Trugilho PF, Abreu Júnior AA, Martinez CLM, Freitas TP. Energy and mass balance in the pyrolysis process of eucalyptus wood. *Cerne* 2018;24:288–94.
- [25] Williams PT, Besler S. The influence of temperature and heating rate on the slow pyrolysis of biomass. *Renew Energy* 1996;7:233–50.
- [26] Wei Q, Qu Y, Tan T. Mass and heat balance calculations and economic evaluation of an innovative biomass pyrolysis project. *Front Chem Sci Eng* 2011;5:355–61.
- [27] Yorgun S, Yildiz D. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. *J Anal Appl Pyrolysis* 2015;114:68–78.

- [28] Pinheiro PCC, Figueiredo FJ, Séye O. Influence of temperature and carbonization heating rate on the properties of Eucalyptus charcoal. *Biomassa Energ* 2005;2:159–68.
- [29] Jesus MS de, Napoli A, Andrade FWC, Trugilho PF, Rocha MFV, Gallet P, et al. Macro ATG kiln: gaseous flow study in the pyrolysis process of Eucalyptus. 2015.
- [30] Zeng K, Minh DP, Gauthier D, Weiss-Hortala E, Nzihou A, Flamant G. The effect of temperature and heating rate on char properties obtained from solar pyrolysis of beech wood. *Bioresour Technol* 2015;182:114–9.
- [31] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007;86:1781–8.
- [32] Anca-Couce A. Reaction mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis. *Prog Energy Combust Sci* 2016;53:41–79.
- [33] Kan T, Strezov V, Evans TJ. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew Sustain Energy Rev* 2016;57:1126–40.
- [34] Wang S, Dai G, Yang H, Luo Z. Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. *Prog Energy Combust Sci* 2017;62:33–86.
- [35] Amutio M, Lopez G, Artetxe M, Elordi G, Olazar M, Bilbao J. Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. *Resour Conserv Recycl* 2012;59:23–31.
- [36] Balat M. Mechanisms of thermochemical biomass conversion processes. Part 1: reactions of pyrolysis. *Energy Sources, Part A* 2008;30:620–35.
- [37] Gremyachkin VM, Mazanchenko EP. Gasification of porous carbon particle by steam. *Russ J Phys Chem B* 2009;3:595–601.
- [38] Puig-Arnavat M, Bruno JC, Coronas A. Review and analysis of biomass gasification models. *Renew Sustain Energy Rev* 2010;14:2841–51.
- [39] Cunliffe AM, Williams PT. Influence of process conditions on the rate of activation of chars derived from pyrolysis of used tires. *Energy & Fuels* 1999;13:166–75.
- [40] Zhai M, Zhang Y, Dong P, Liu P. Characteristics of rice husk char gasification with steam. *Fuel* 2015;158:42–9.
- [41] Molino A, Larocca V, Chianese S, Musmarra D. Biofuels production by biomass gasification: A review. *Energies* 2018;11:811.
- [42] Pattar NK, Gowreesh SS. Tar formation, reduction and technology of tar during biomass gasification/pyrolysis—an overview. *Int J Eng Res Technol IJERT* 2017;6:62–70.
- [43] Ersöz A, DurakÇetin Y, Sarioğlan A, Turan AZ, Mert MS, Yüksel F, et al. Investigation of a novel & integrated simulation model for hydrogen production from lignocellulosic biomass. *Int J Hydrogen Energy* 2018;43:1081–93.
- [44] Pallozzi V, Di Carlo A, Bocci E, Villarini M, Foscolo PU, Carlini M. Performance evaluation at different process parameters of an innovative prototype of biomass gasification system aimed to hydrogen production. *Energy Convers Manag* 2016;130:34–43.
- [45] Gupta A, Dasappa S. Hydrogen from Biomass by Oxy-Steam Gasification-A Quantitative Analysis of Cases. *Proc. 26th Eur. Biomass Conf. Exhib.*, vol. 623, 2018, p. 14–7.
- [46] Wong JWC, Tyagi RD, Visvanathan C, Hua Yan J, Selvam A. Special issue on 'Advanced treatment technologies for waste recycling': selected papers from the 'International Conference on Solid Waste-Moving Towards Sustainable Resource Management', 2-6 May 2011, Hong Kong Sar. *Environ Technol* 2012;33:2479.
- [47] Hirano A, Hon-Nami K, Kunito S, Hada M, Ogushi Y. Temperature effect on continuous gasification of microalgal biomass: theoretical yield of methanol production and its energy balance. *Catal Today* 1998;45:399–404.
- [48] Corella J, Aznar MP, Caballero MA, Molina G, Toledo JM. 140 g H₂/kg biomass daf by a CO-shift reactor downstream from a FB biomass gasifier and a catalytic steam reformer. *Int J Hydrogen Energy* 2008;33:1820–

6.

- [49] Susmozas A, Iribarren D, Zapp P, Linßen J, Dufour J. Life-cycle performance of hydrogen production via indirect biomass gasification with CO₂ capture. *Int J Hydrogen Energy* 2016;41:19484–91.
- [50] Holt JA, Yost MA, Winward D, Creech JE, Allen LN, McAvoy D. Biochar had minor effects on yield, quality, and water availability of irrigated alfalfa, corn, and wheat. *Agron J* 2022;114:1717–30.
- [51] Polat H, Molva M, Polat M. Capacity and mechanism of phenol adsorption on lignite. *Int J Miner Process* 2006;79:264–73.
- [52] Tibor ST, Grande CA. Industrial production of activated carbon using circular bioeconomy principles: Case study from a Romanian company. *Clean Eng Technol* 2022;7:100443.