



**EFFECT OF MINERAL MATTER REMOVAL ON PYROLYSIS OF
WOOD SAWDUST FROM AN INVASIVE SPECIES**

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10 **EFFECT OF MINERAL MATTER REMOVAL ON PYROLYSIS OF WOOD**
11 **SAWDUST FROM AN INVASIVE SPECIES**
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Abstract

Kinetics of the pyrolysis of wood sawdust from the invasive species *Parkinsonia aculeata*, untreated and demineralized by a mild acid treatment, is comparatively investigated in order to examine the effect of the removal of minerals naturally present in the biomass. Non-isothermal thermogravimetric analysis from room temperature up to 500 °C is applied for this purpose. Demineralization shifts the process onset and the maximum degradation rate to higher temperatures, and leads to enhance the activation energy from 56 kJ mol⁻¹ to 60 kJ mol⁻¹, pointing to a catalytic role of alkaline and alkaline earth metals in the biomass. Likewise, the three kinds of pyrolysis products (gas, bio-char and bio-oil) are obtained from experiments performed in a bench-scale installation at 500 °C. Yields and physicochemical characteristics of the pyrolysis products are determined. The pronounced reduction in the content of metals in the sawdust leads to increase bio-oil yield in around 10%, the specific surface area of the bio-char, from $\approx 2 \text{ m}^2\text{g}^{-1}$ to $\approx 74 \text{ m}^2\text{g}^{-1}$, and the higher heating value of all the pyrolysis products.

Keywords: *invasive wood biomass, pyrolysis, bio-energy, bio-fuels, bioresources*

1. Introduction

Depletion of fossil fuels and worldwide public concern about the detrimental effects of environmental pollution related to their use on human health and climate change have deepened the interest in biomass utilization, due to its renewable character and net carbon neutral energy conversion. Bioenergy offers cost-effective and sustainable opportunities with the potential to meet 50% of world energy demands during the next century, contributing to reduce carbon emissions from fossil fuels and to mitigate climate change (Chew and Doshi, 2011; Qu et al., 2011).

Growing demand of biomass, mainly of residues from conventional wood, such as sawdust, shavings and chips, for heat and power production has led to the search of other biomasses, which include agro-residues, wastes from the food industry, and energy crops. Among alternative biomass resources, invasive wood species have been almost unexplored. Conversion of biomass from these wood species by pyrolysis, a key thermochemical processes, may constitute an interesting option to generate bioenergy and other valuable products. It could contribute to control their expansion and to lower costs related to soil adaptation (De Lange et al., 2012). In particular, *Parkinsonia aculeata* is a major invasive arboreal species in several regions worldwide. It forms dense thickets, preventing access for humans, native animals and livestock to waterways. The seedpods float, and the plant spreads by dropping pods into water, or pods are washed downstream by seasonal flooding (Nunell et al., 2012).

Within this framework, the present study deals with kinetic characterization of the pyrolysis of *P. aculeata* wood sawdust, which is relevant for the reliable design of full-scale units, as well as with determination of main properties of the three kinds of pyrolysis products to assess their potential applications. Special emphasis is given to the

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3 effect of the removal of mineral matter inherently present in the sawdust, since
4 minerals, particularly salts or oxides of alkaline and alkaline earth metals, may affect
5 the thermal degradation mechanism of biomass and modify characteristics of the
6 pyrolysis products (Di Blasi et al., 2009; Eom et al., 2012). Minerals removal is also
7 important from a technological viewpoint due to adverse effects related to their presence
8 on biomass thermochemical conversion, including fouling, slagging, and ash
9 agglomeration, among others (González et al., 2008).
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20 **2. Experimental section**

21 **2.1. Biomass pretreatment**

22 *Parkinsonia aculeata* debarked trunks were obtained from a rural area located in
23 Buenos Aires province, Argentina. They were sun dried, crushed, milled, and screen-
24 sieved. Fractions of particle diameter between 250 μm and 500 μm were reserved for
25 chemical characterization. For mineral matter removal, sawdust samples were treated
26 with a 10 wt% HCl acid solution (20 mL/g of sample) at 80 °C for 1 h. The acid-treated
27 samples were subsequently rinsed with distilled water until almost neutral pH in
28 washing water was attained. Afterwards, they were filtered and dried up to constant
29 weight. The untreated and demineralized sawdust samples are labeled as US and DS,
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48 **2.2. Pyrolysis experiments**

49 Kinetic measurements for the pyrolysis of US and DS were conducted in a
50 simultaneous thermal analyzer (TG-DSC/DTA TA Instruments SDT Q600) equipped
51 with a N₂ flow device and a data acquisition system. Each sample was thermally treated
52 under flowing N₂ from ambient temperature up to 500 °C. Experiments were carried out
53 for samples' masses of 10 mg, fractions of 44-74 μm particle diameter, and heating rate
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3 of 10 °C/min. For these conditions, negligible diffusional effects were thoroughly
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5 verified. Furthermore, to examine the effect of mineral matter removal on yield and
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7 characteristics of the pyrolysis products, experiments were performed in a bench-scale
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9 installation under pre-established operating conditions ($T = 500\text{ °C}$, N_2 flow rate = 200
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11 mL min^{-1} , particle diameter = 250-500 μm ; reaction time = 30 min). The equipment
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13 mainly consisted of a stainless steel fixed-bed reactor (2.6 cm O.D., 110 cm total length)
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15 externally heated by an electrical furnace driven by a programmable temperature
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17 controller, feed and control systems. At the reactor outlet, a series of flasks immersed in
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19 a cooling bath, using isopropyl alcohol at -10 °C as solvent, enabled condensation and
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21 collection of the condensable volatiles generated with pyrolysis course.
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25 The residual solid and the accumulated liquid products contained in the flasks
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27 were weighed to determine product yields. These products were then carefully stored in
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29 closed containers for further characterization. Gas yields were obtained by difference
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31 from overall mass balances. Each experiment was repeated three times and averaged
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33 values are reported with a standard deviation (SD) less than 5%.
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38 2.3. Analytical methods

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40 Proximate and elemental analyses of US and DS were carried out by
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42 conventional ASTM standards and using a Carlo Erba Fisons EA1108 CHNS-O
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44 instrument, respectively. Soxhlet extraction with ethanol/toluene (1:2 v:v) was also
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46 applied to both samples, following TAPPI T 204 om-88. The samples free of extractive
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48 components were then treated with 72% H_2SO_4 in order to quantify lignin (TAPPI T222
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50 om-02). The content of holocellulose (cellulose + hemicellulose) was determined by
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52 subtracting the lignin content from the weight of the extractive-free samples. In
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54 addition, ash composition of US and DS were determined by atomic absorption
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3 spectrophotometry using a Perkin Elmer Analyst 200 instrument supplied with hollow
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5 cathode lamps for each element.
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7 Non-condensable gases, after flowing through the condensation system, were
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9 sampled periodically using Teflon gas bags, and further analyzed with a Shimadzu GC-
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11 8 gas chromatograph supplied with a thermal conductivity detector and a concentric
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13 packed Altech CTR I column (6 ft x ¼ in). Argon as carrier gas and a temperature of 25
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15 °C were employed.
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18 Chemical characteristics of the char and the bio-oil were determined by
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20 proximate and/or ultimate analyses, as depicted above. Density of the bio-oils was
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22 assessed from measurements by picnometry at 20°C, while their pH was determined
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24 with an Orion 290A portable pH meter. Besides, for the char, surface properties were
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26 assessed from N₂ (-196 °C) adsorption isotherms obtained with a Micromeritics ASAP
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28 2020 HV surface analyzer, following conventional procedures earlier reported (Basso
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30 and Cukierman, 2006; Bonelli et al., 2012). The BET procedure was applied to evaluate
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32 the specific surface area (S_{BET}). Total pore volume (V_T) was obtained from the N₂
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34 volume adsorbed at the highest relative pressure, and average pore radius was calculated
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36 as $r = 2 V_T/S_{BET}$. On the other hand, higher heating value (HHV) of the generated char
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38 and bio-oil was also measured using a Parr 1341 oxygen bomb calorimeter.
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45 3. Results and discussion

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47 Chemical characteristics of the untreated and demineralized samples are shown
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49 in Table 1. Results from proximate and elemental analyses of US are similar to those
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51 reported for hardwoods (Saidur et al., 2011). The results in Table 1 show that the acid
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53 treatment was effective in removing more than 85% of the mineral matter, as inferred
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55 from the reduction in ash content of the DS. It also led to increase volatile matter and
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3 %C, and to decrease %O. The trend agrees with results reported for other
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5 lignocellulosic biomasses (Fahmi et al., 2008). In turn, increase in the lignin content of
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7 the DS may be attributed to acid hydrolysis of hemicellulose (Eom et al., 2012).
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9 Besides, Table 2 shows the contents of major metals in the ashes of US and DS.
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11 Comparison of the results for US and DS enabled to verify acid treatment effectiveness,
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13 pointing to a pronounced decrease in the contents of alkaline and alkaline earth metals
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15 in agreement with other reported results (Shi et al., 2012). As silicon and iron were
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17 almost unaffected by the acid treatment, the content of these metals in the ashes
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19 increased relatively.
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23 Figure 1 shows TG curves and pyrolysis rate profiles for the thermal degradation
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25 of the untreated and demineralized sawdust. Instantaneous ash-free weight fractions (W)
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27 and pyrolysis rates ($-dW/dt$) are represented as a function of the temperature. The latter
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29 were obtained by differentiation of weight fractions-time curves. The acid treatment
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31 modified the pyrolytic behavior of the sawdust leading to enhance thermal stability of
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33 the demineralized sample, as evidenced from the higher onset degradation temperature.
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35 The maximum degradation rate shifted to a higher temperature, from 350 °C to 370°C,
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37 and attained a higher value (0.067 min^{-1} for US against 0.125 min^{-1} for DS) due to the
38
39 applied treatment. The temperature range for which the main weight loss takes place
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41 was reduced. The residual weight fraction (W_r) at the highest temperature for DS
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43 attained a lower value ($W_r = 0.25$) than that for US ($W_r = 0.21$), in line with the greater
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45 content of volatile matter determined for the former (Table 1). The behavior could be
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47 due to catalytic effects, especially of alkaline and alkaline earth metals in the sawdust
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49 (Table 2), on the secondary reactions taking place between the primary products,
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51 involving re-polymerization of the tars in the vapor phase, which might lead to increase
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53 the solid product yield (Raveendran et al., 1995).
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To evaluate the kinetic parameters for the pyrolysis of the US and DS, modeling of the TG curves was carried out. The simple model which assumes pyrolysis as a first-order overall decomposition and the usual Arrhenius type dependence of the rate constant on temperature, was applied:

$$-dW/dt = k_0 \exp(-E_A/RT)(W - W_r) \quad (1)$$

W and W_r in Eq. (1) are the instantaneous and residual weight fractions, respectively; k_0 is the pre-exponential factor, E_A , the activation energy, R , the universal gas constant, and T , the absolute temperature. Model characteristic parameters (k_0 , E_A) were evaluated by non-linear regression analysis. Removal of the mineral matter led to increase the activation energy, from 56 kJ mol⁻¹ to 60 kJ mol⁻¹, indicating that the presence of minerals in the sawdust could catalyze its thermal degradation. The pre-exponential factor also increased from 5x10³ min⁻¹ to 1.1x10⁴ min⁻¹. Model predictions are also included in Figure 1. As seen, the model enabled to represent properly the kinetic data over the temperature range investigated.

Yields of the three kinds of the pyrolysis products generated from the US and DS are comparatively shown in Figure 2. Yields of the bio-oil and bio-char were 36.1% and 25.8% for US, and 45.9% and 18.3% in the case of DS, respectively. According to mass balance closure, the gas yields were 38.1% for US and 35.9% for DS. Mineral matter removal led to increase bio-oil yield, at the expense of decreases in yields of the bio-char and gas. Enhancement in bio-oil yield agrees with results reported for the pyrolysis of some other demineralized lignocellulosic biomasses (González et al., 2008; Shi et al., 2012). Table 3 shows characteristics of the solid and liquid products generated from the pyrolysis of US and DM. Density and pH values of the bio-oils are comparable to those typically reported for conventional wood-derived crude bio-oil

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3 (Bridgwater, 2012). Demineralization led to enrichment in %C and %H of the bio-char
4 and bio-oil, in turn resulting in higher HHV of both products. It also intensified pore
5 development of the bio-char, primarily dependent upon volatile matter release, as
6 inferred from the enhanced BET surface and total pore volume of the DS bio-char, and
7 led to reduce the average pore radius, pointing to a bio-char with a more microporous
8 structure. The greater content of volatiles of the DS and the lower residence time of
9 volatiles due to the increase in the reaction rate for temperatures above 325 °C (Figure
10 1) could explain the enhancement in pore structure development (González et al., 2008).
11 The DS bio-char could be used as rough adsorbent, soil enhancer and CO₂ capture agent
12 in soil, and/or as intermediate product to obtain activated carbon by steam or CO₂
13 gasification.
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27 Cumulative fractions of major gaseous species generated from the pyrolysis of
28 US and DS are shown in Figure 3. CO₂ was the main gaseous species generated from
29 US pyrolysis, followed in decreasing order by CH₄, CO, and H₂. As seen, minerals
30 removal induced a pronounced reduction of CO₂, suggesting that alkaline and alkaline
31 earth metals in the US promote reactions that facilitate CO₂ formation, mainly
32 decarboxylation and decarbonylation (Shi et al., 2012). These reactions should be less
33 favored for the pyrolysis of DS due to its lower content of metals (Table 2), while those
34 leading to CH₄ formation, mainly ascribed to the cracking of methoxy-O-CH₃ groups
35 (Qu et al., 2011), should become more important. To evaluate the HHV of the gas
36 produced, total yield of each gaseous species was first obtained by integration of the
37 instantaneous yield over the reaction time. The following expression, which takes into
38 account the combustion heat of each gas, was then applied where G_i represents the total
39 moles produced per unit mass of biomass:
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$$56 \text{ HHV [MJ/kg]} = 0.802 G_{\text{CH}_4} + 0.286 G_{\text{H}_2} + 0.283 G_{\text{CO}} \quad (2)$$

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3 Minerals removal led to enhance the HHV of the gas, from 1.3 MJ/kg of untreated
4 biomass to 3.4 MJ/kg of demineralized biomass. The increase in HHV may be attributed
5 to the greater fraction of CH₄ and CO composing the gas generated from the pyrolysis
6 of the demineralized sawdust.
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11 12 13 14 **4. Conclusions**

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16 Wood sawdust from the invasive species *Parkinsonia aculeata* represents an
17 attractive, alternative biomass resource for its conversion into valuable energy products
18 through pyrolysis. Mineral matter removal enhances the process activation energy,
19 pointing to a catalytic role of alkaline and alkaline earth metals present in the sawdust. It
20 could favor potential applications of the pyrolysis products, leading to increase the yield
21 of bio-oil and the HHV of the three kinds of pyrolysis products. The bio-oil shows
22 similar fuel characteristics to those obtained from conventional wood-derived crude bio-
23 oils, whereas the gas might contribute to energy sustainability of the process. In turn,
24 the bio-char from the demineralized sawdust has potential as environmentally friendly
25 solid bio-fuel, inexpensive rough adsorbent, soil enhancer and CO₂ capture agent in soil,
26 and/or as intermediate product for further conversion into activated carbon.
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41 42 43 **Acknowledgments**

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Table 1. Chemical characteristics of the untreated and demineralized sawdust samples.

Characteristic / Sample	US	DS
<u>Proximate analysis</u> ^(a) (wt%)		
Volatile matter	77.4	79.5
Ash	1.4	0.2
Fixed carbon ^(b)	21.2	20.3
<u>Elemental analysis</u> ^(c) (wt%)		
Carbon	48.0	51.0
Hydrogen	5.7	5.7
Nitrogen	0.2	0.3
Oxygen ^(b)	46.1	43.0
<u>Biopolymers contents</u> ^(d) (wt%)		
Lignin	24.1	39.6
Holocellulose ^(b)	75.9	60.4

^(a) dry basis; ^(b) estimated by difference; ^(c) dry and ash free basis; ^(d) dry and extractive free basis. The SD did not exceed 5%.

Table 2. Ash composition of untreated (US) and demineralized sawdust (DS).

Content (mg/kg)	Na	K	Mg	Ca	Al	Fe	Si
US	106900	53200	57300	236600	14300	6900	118800
DS	30400	32500	5100	58900	4100	22400	345000

The SD did not exceed 5%.

Table 3. Characteristics of the bio-char and bio-oil from the pyrolysis of the untreated (US) and demineralized sawdust (DS).

Characteristic / Sample	US char	DS char	US bio-oil	DS bio-oil
<u>Proximate analysis</u> ^(a) (wt%)				
Volatile matter	19.3	18.9	-	-
Fixed carbon ^(b)	74.9	80.4	-	-
Ash	5.8	0.7	-	-
<u>Ultimate analysis</u> ^(c) (wt%)				
Carbon	79.6	82.3	53.4	58.3
Hydrogen	2.0	2.8	5.4	6.7
Nitrogen	0.5	0.9	1.4	0.7
Oxygen ^(b)	22.6	14.2	39.8	34.3
HHV (MJ/kg)	26.7	30.4	20.5	23.7
pH	-	-	3.15	2.54
Density (g/cm ³)	-	-	1.00	0.98
<u>Surface properties</u>				
S _{BET} (m ² /g)	1.6	73.8	-	-
V _T (cm ³ /g)	0.01	0.04	-	-
r (nm)	1.4	0.2	-	-

^(a) dry basis; ^(b) estimated by difference; ^(c) dry and ash free basis. The SD did not exceed 5%.

Figures' Captions

Figure 1. Thermogravimetric curves and reaction rate profiles for the pyrolysis of the untreated (US) and demineralized sawdust (DS). Comparison between experimental data (points) and kinetic model predictions (lines).

Figure 2. Product yields for the pyrolysis of the untreated and demineralized sawdust samples at 500 °C.

Figure 3. Composition of the gas generated from the pyrolysis of the untreated sawdust (US) and demineralized sawdust (DS) at 500°C.

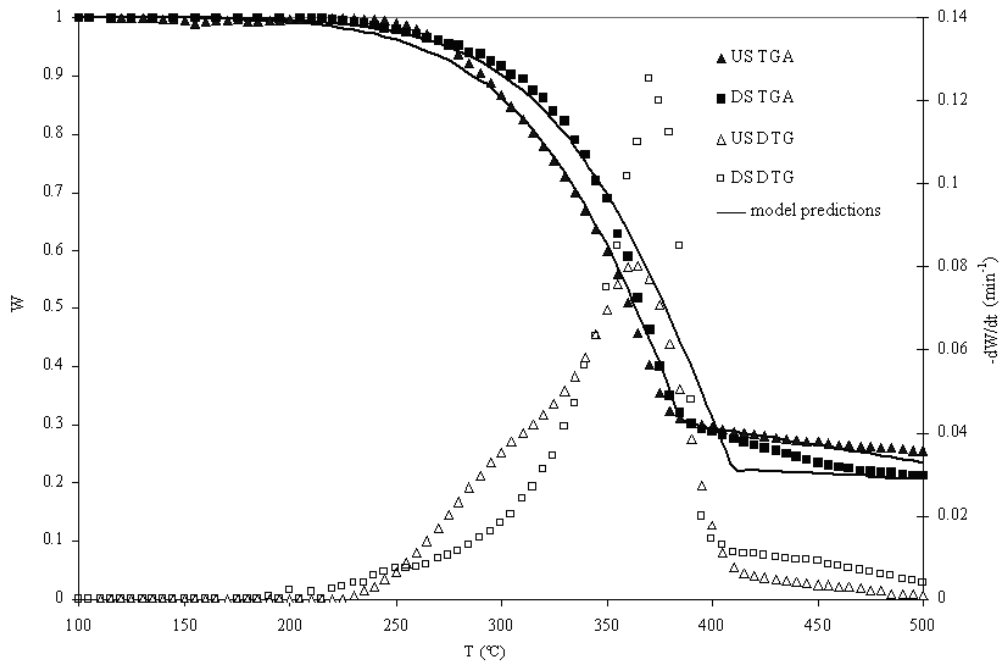


Figure 1

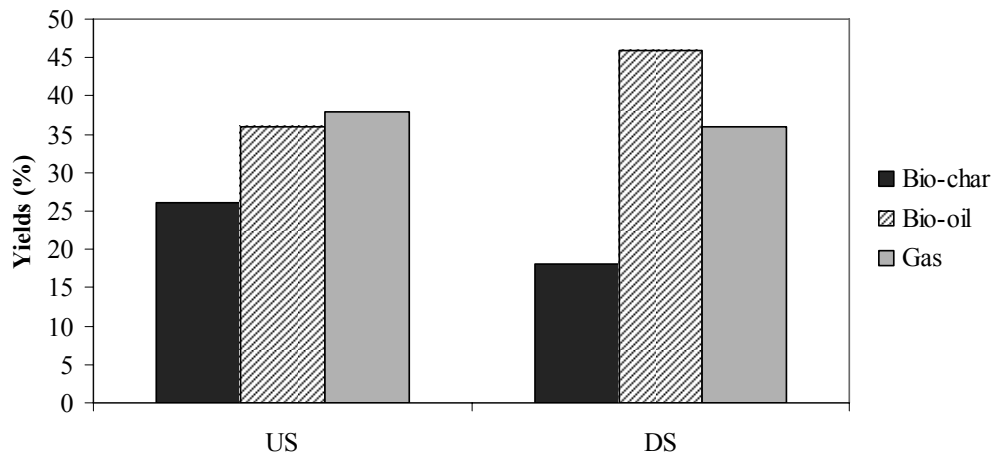


Figure 2

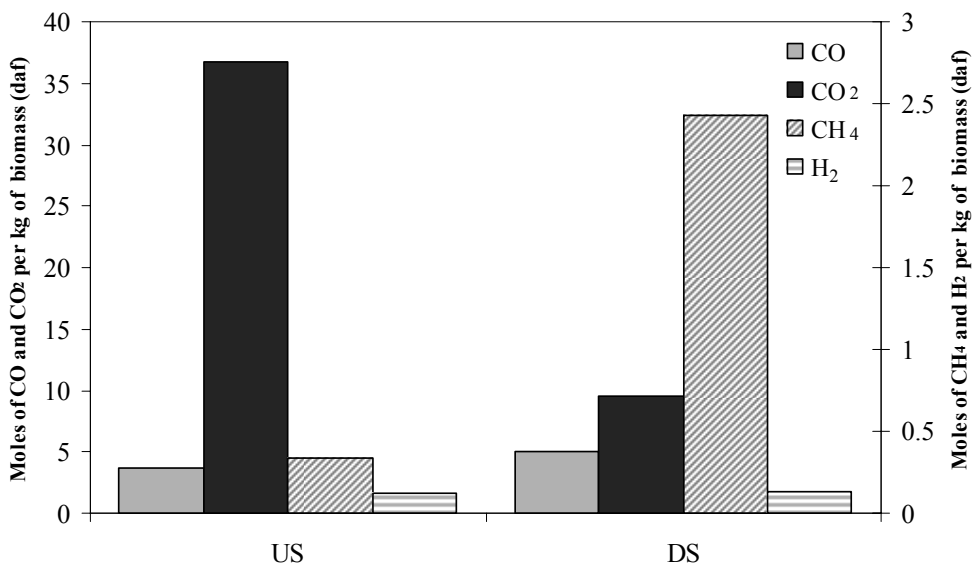


Figure 3

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