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# Hydrothermal carbonization of coniferous biomass: effect of process parameters on mass and energy yields

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**Abstract:** Hydrothermal carbonization of biomass presents a promising way to improve fuel characteristics of biomass without preliminary drying. In this process, feedstock is subjected to heating with water at temperatures between 180 – 250 °C during a certain period of time. This paper investigates the effect of process conditions (temperature, time, and the ratio between biomass and water) on the hydrothermal carbonization of coniferous biomass. Three sets of experiments were carried out with coniferous wood chips. Mass and energy yields together with proximate analysis measurements were used for the carbonization process evaluation. Dependencies of hydrochar mass and energy yields from the operation parameters could be described with mathematical correlations.

**Keywords:** hydrothermal carbonization; coniferous biomass; energy densification

## 1 Introduction

The use of biomass fuels is currently quite intensively promoted as one way of reducing carbon dioxide emissions. Wood and other forms of biomass present a perspective source to substitute conventional fossil fuels with zero net CO<sub>2</sub> emissions [1, 2]. Using biomass as fuel is associated with certain difficulties, however. The heterogeneity of properties, low density, poor grindability, relatively high moisture content, and hydrophilic behavior - all these factors increase the cost of biomass applications [2–7].

Hydrothermal carbonization (HTC) is a relatively recent technology that offers the benefits of converting the biomass into homogenous lignite-like material. In this process, biomass in a mixture with water is kept during a certain period of time in a closed vessel in the temperature range of 180 – 250 °C (pressure corresponding saturated values). [2, 8–12] The reaction temperature, residence time, and water-to-biomass (w/b) mass ratio are reported to be the main factors to determine the rate of wood components decomposition [2, 11, 12]. Several reaction mechanisms are involved in biomass decomposition during HTC, such as hydrolysis, dehydration, decarboxylation, polymerization, and aromatization. Components of lignocellulosic biomass (lignin, hemicellulose, and cellulose) become less stable with the presence of water under saturated conditions [2, 4, 13].

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Solids (hydrochar), aqueous solution, and some amount of gases (about 10% by mass of feedstock) are generated during the HTC process. Hydrochar presents the main product of the process. In comparison with the feedstock, hydrochar is characterized by the increased carbon content [4, 7, 8, 10], higher homogeneity, better grindability, and hydrophobic behavior [4, 5, 11, 14]. These improved product characteristics together with the independence from feedstock moisture make the HTC process a promising technology for enhancing biomass fuel properties. Besides the utilization for heat and power production, hydrochar may find other potential applications: for example soil fertilizer, catalyst, energy storage, or absorbent [13, 15].

Recent studies mostly report on HTC activities with deciduous wood (beech [14], poplar [11, 16], bamboo [6]), herbaceous biomass (agricultural residues [17], sunflower stem [2], wheat [18], and barley straw [10]) as well as with non-lignocellulosic materials (algae [12, 19], MSW [20], packaging materials [21], and digestate [18]). So far, the results on the hydrothermal carbonization of coniferous biomass are limited to experiments with loblolly pine [4, 19] and white fir/Jeffrey pine (Tahoe mix) [5].

Coniferous and deciduous wood have certain differences in the chemical composition and amount of lignocellulosic components [22, 23]. During hydrothermal carbonization, hemicellulose as the most reactive wood cell fraction is mainly affected. At the same time, previous research indicated that in coniferous wood this component is mannan-based, while deciduous species are rich with more reactive xylan-containing fractions. For this reason, the reactivity of hemicelluloses and decomposition character together with distribution and characteristics of resulting products noticeably differ between coniferous and deciduous wood. [9, 22, 23] Therefore, previously published results on the deciduous wood decomposition during HTC could not be directly applied for coniferous species. The main objective of this work was to gather more experimental data on the hydrothermal carbonization of coniferous wood. Wood chips and hydrochar samples were characterized by proximate analysis measurements. The influence of process parameters (temperature, time, and water-to-biomass ratio) on hydrochar mass and energy yields was evaluated and described with mathematical correlations.

## **2 Materials and methods**

### **2.1 Feedstock material**

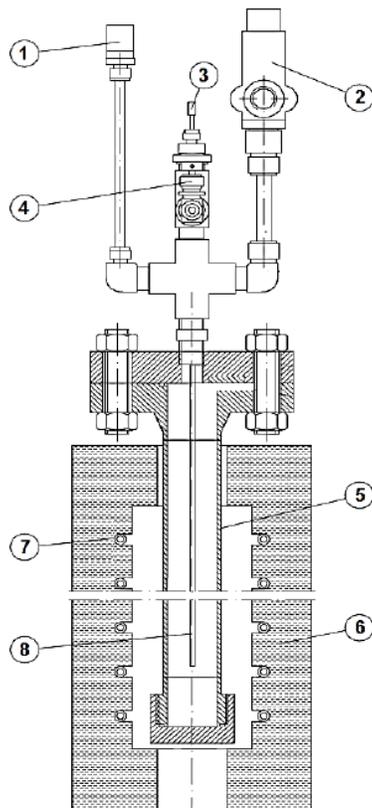
Wood chips from coniferous species presented by pine and different logging residues were collected locally (Lappeenranta, Finland) and used for experiments. The material was milled to the particle size of 1 cm in length on average and air dried. Before the experiments, biomass was kept in plastic bags at room temperature. Figure 1 presents an example of feedstock material.



**Figure 1.** Milled wood chips for experiments.

## 2.2 HTC reactor

Hydrothermal carbonization was performed in a batch reactor designed and constructed at Lappeenranta University of Technology (Lappeenranta, Finland). The 1 L reactor is comprised of a stainless steel tube with a flange connection at the top part and screw closing at the bottom (Fig. 2). Heat to the process was provided by a controllable 10 kW electric heater coil surrounding the reactor tube. The experimental unit was covered by a thick insulation layer and outer steel sheet.



**Figure 2.** HTC experimental unit, where (1) pressure sensor; (2) safety valve (set point pressure 40 bar, maximum temperature 300 °C); (2) reactor tube; (3) thermocouples;

(4) sampling valve (maximum temperature 315 °C, maximum pressure 215 bar); (5) reactor tube; (6) insulation; (7) heater; (8) thermocouples.

Two thermocouples were used to monitor the temperatures at the lower and upper zones of the reactor (at 245 mm and 645 mm from the top). Pressure sensor and pressure relief valve were set at the top of the unit. The required temperature level inside the reactor during the desired period of time was maintained with a proportional-integral-derivative (PID) controller. Data from the temperature and pressure sensors was recorded automatically every 2 seconds.

### 2.3 Experimental procedure

In the current work, three sets of HTC experiments were performed. Water-to-biomass mass ratios of 6:1 (approximately 50 g of fuel and 300 ml of water) and 8:1 (approximately 50 g of wood and 400 ml of water) were tested. Residence times of three and six hours were used in the experiments. The reaction temperature was varied in the range of 180 - 250 °C. The principle biomass components became more reactive under the saturated conditions within this temperature range: not only hemicellulose that is completely decomposed around 230 °C, but also typically more stable cellulose and lignin reacted partially at this temperature [7, 9].

For each experiment, a pre-weighted sample of biomass was dispersed in water and stirred manually. At the end of the experiment, the carbonized wood and liquid products were collected and then separated by vacuum filtration using the Büchner funnel with a Whatman glass microfiber filter paper (grade GF/A). Hydrochar was subsequently dried overnight in the oven at a temperature of  $105 \pm 2$  °C. All tests were performed at least twice, and the average values were chosen. Liquid and gaseous product analysis was not included in the scope of the current work.

Hydrochar samples were named in accordance with the operation parameters as HTC- $t$ - $r$ , where  $t$  denotes the reaction time and  $r$  the w/b ratio.

### 2.4 Analytical methods

Both raw and carbonized biomasses were characterized by proximate analysis and heating value measurements in accordance with standard procedures. Each sample was analysed at least twice, and the average value was utilized.

According to the standard SFS EN 14775:2009 [24], the percentage of ash in solid biofuel could be found as a mass of the inorganic residual after heating the biomass in air under controlled time and temperature conditions (550 °C at the maximum). The procedure for defining volatile matter is described in the standard SFS EN 15148:2009 [25]. Biomass sample mass loss after maintaining the sample for seven minutes at the temperature of  $900 \pm 10$  °C without contact with air refers to volatiles. The moisture was determined with the moisture meter Sartorius 7093.

The higher heating value was measured with the Parr 6400 calorimeter. Fuel samples were ground to powder and pelletized with a pellet press before being placed in the calorimeter.

### 3 Results and discussion

#### 3.1 Biomass characterization

Dried hydrochar samples from the experiments with the w/b ratio of six and the residence time of six hours are presented in Fig. 3. The colour of wood changes significantly with the process temperature increase: from light brown at lower temperatures to dark brown/black at higher temperatures. This colour change presents a visual demonstration of substantial changes in wood cell components [10, 27].



**Figure 3.** Hydrochar samples (reaction time = 6 hours, w/b ratio = 6).

The results of proximate analysis and higher heating values for wood chips before and after HTC tests are presented in Table 1. Initially, feedstock material has a relatively high fraction of volatiles and low ash content. Such values are quite typical for woody biomass [26]. Hydrothermal carbonization significantly decreases the moisture content of biomass due to the decomposition of lignocellulosic components [9, 27]: the moisture of the hydrochar samples from all experiments is on average 80 % lower than the original value. During the HTC process, some part of the ash forming minerals are dissolved in the water [19, 28], and this results in the decrease of hydrochar ash content at low reaction temperatures (for hydrochars at 180 °C, the ash content is around 0.24%). At the same time, with the carbonization rate increase, a higher amount of ash remains in the hydrochar: the ash contents for HTC-3h-6, HTC-6h-6, and HTC-3h-8 at 250 °C are 0.59%, 0.77%, and 1.07%, respectively. Obtained experimental results are quite consistent with the published data [2, 27, 29].

The reactions of decomposition during HTC resulted in the loss of volatile compounds with a simultaneous increase in the fixed carbon content. Biomass loses more volatiles with higher temperatures and longer residence times: the hydrochar volatile content in the case of HTC-6h-6 at 250 °C is 45.2% (almost half of the initial value). Conversely, the fixed carbon content increases with temperature as volatiles are removed: biomass

samples after HTC at 250 °C have approximately six times higher fixed carbon contents than the feedstock material.

**Table 1.** Proximate analysis and heating values for hydrochar samples and wood chips.

Time [h] / water/biomass ratio [-]		Reaction temperature [°C]				
		180	200	220	240	250
3 / 6	M [%]	1.00	2.55	2.45	1.90	2.45
	VM [%]	79.03	70.45	61.01	54.70	49.94
	A [%]	0.24	0.28	0.45	0.71	0.59
	FC [%]	19.73	26.72	36.10	42.69	47.02
	HHV <sub>dry</sub> [MJ/kg]	21.95	23.89	25.66	27.17	27.94
6 / 6	M [%]	1.20	1.20	1.90	1.95	1.75
	VM [%]	71.71	61.40	57.04	49.84	44.18
	A [%]	0.22	0.88	0.58	0.64	0.77
	FC [%]	26.86	36.52	40.48	47.58	53.30
	HHV <sub>dry</sub> [MJ/kg]	23.18	24.74	26.40	28.00	28.81
3 / 8	M [%]	1.20	1.20	1.55	1.75	2.10
	VM [%]	72.93	68.83	60.27	51.51	45.19
	A [%]	0.27	0.32	0.50	0.47	1.07
	FC [%]	25.61	29.64	37.68	46.27	51.64
	HHV <sub>dry</sub> [MJ/kg]	22.73	24.47	25.79	27.38	28.36
Feedstock	M [%]	8.00				
	VM [%]	82.60				
	A [%]	0.74				
	FC [%]	8.66				
	HHV <sub>dry</sub> [MJ/kg]	20.52				

M: moisture; VM: volatile matter; A: ash; FC: fixed carbon; HHV<sub>dry</sub>: higher heating value on dry basis.

In the experiments with walnut shell and sunflower stem by Román et al. [2], the difference in the residence time (20–45 hours) appears to have no effect on the process products distribution. This can be explained by relatively long residence times that ensure complete hemicellulose and significant cellulose decomposition. Current results show that all investigated process parameters have an influence on the carbonization rate within the studied limits.

## 3.2 Mass and energy yields of hydrochar

### 3.2.1 Hydrochar mass yield

The mass yield ( $MY$ ) [-] was defines as:

$$MY = \frac{mass_{hydrochar}}{mass_{biomass}} \quad (1)$$

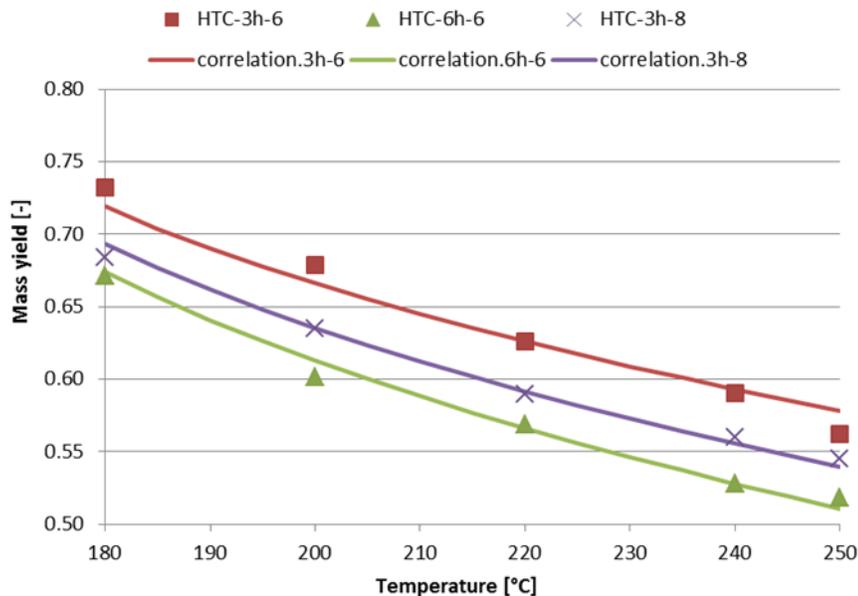
where  $mass_{hydrochar}$  [kg] is the dry mass of hydrochar and  $mass_{biomass}$  [kg] is the dry mass of biomass used for the experiment.

A number of different equation forms were trialled to describe the obtained results for the mass yield. The following correlation with the constants calculated by minimizing the residual sums of squares (RSS) demonstrated the most accurate results:

$$MY = 1 - 0.04079(T - 150)^{0.337} t^{0.2142} r^{0.3055} \quad (2)$$

where  $T$  [°C] is the process temperature,  $t$  [h] is the residence time, and  $r$  [-] is the w/b ratio.

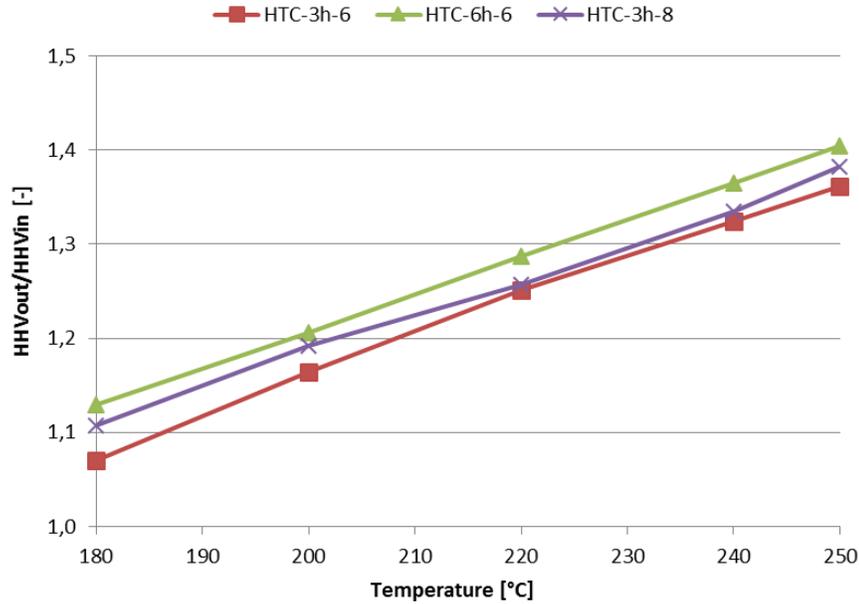
Figure 4 illustrates the experimental results together with the correlation curves for the hydrochar mass yield. The tendencies observed are quite consistent with the published data for coniferous biomass [4, 5]. The increase of reaction temperature leads to a significant decrease of solid yield: for all three experimental sets, increasing the temperature from 180 °C to 250 °C reduced the mass yield on average by 20 %. A higher water-to-biomass ratio causes a relatively slight increase of solid mass loss, which can be due to the greater effect of water in the hydrolysis reaction [2]. Within the investigated parameters, longer residence times resulted in more complete carbonization and, as a consequence, lower mass yields.



**Figure 4.** Hydrochar mass yield: experimental results and correlation curves (Eq. (2)).

### 3.2.2 Hydrochar energy yield

Figure 5 illustrates the effect of process parameters modifications on the heating value of hydrochar. The biggest growth of energy content corresponds to the highest reaction temperatures for all three series of experiments: hydrochar heating value is approximately 40% higher at 250 °C than the initial one. Such value is consistent with the results reported in literature [2, 5, 8, 9].



**Figure 5.** Relative increase of hydrochar heating value.

The hydrochar energy yield ( $EY$ ) [-] was calculated with Eq. (3):

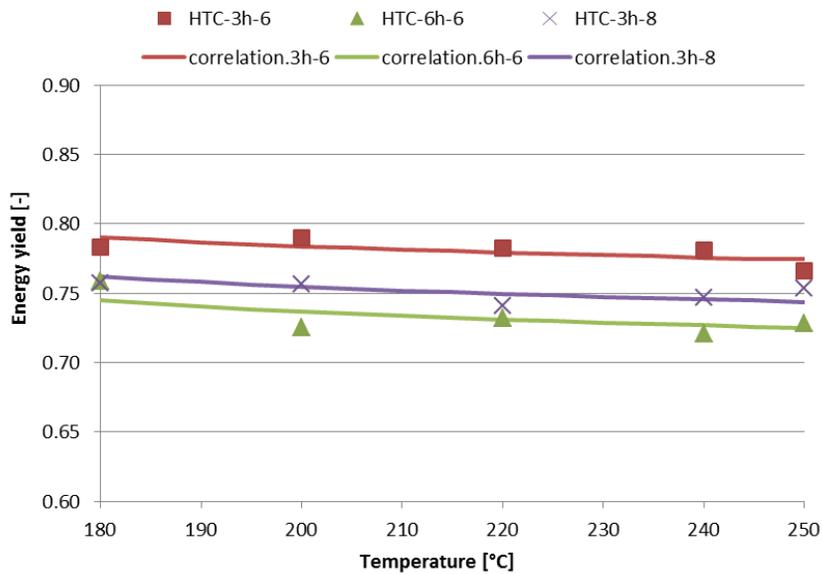
$$EY = MY \cdot \frac{HHV_{out}}{HHV_{in}} \quad (3)$$

where  $HHV_{out}$  [MJ/kg] is the higher heating value of hydrochar (dry basis) and  $HHV_{in}$  [MJ/kg] is the higher heating value of biomass (dry basis).

The following correlation was used to describe the experimental results for energy yield with satisfactory accuracy (the constants were calculated by minimizing the RSS):

$$EY = 1 - 0.05632(T - 150)^{0.062} t^{0.2846} r^{0.4405} \quad (4)$$

The experimental results and corresponding correlation curves for hydrochar energy yield are presented in Fig. 6. As can be expected, the correlation for the energy yield resembles the correlation for the hydrochar mass yield from Eq. (2). This implies that the mechanisms of feedstock mass loss and hydrochar energy densification during HTC have the similar character but somewhat different rates.



**Figure 6.** Hydrochar energy yield: experimental results and correlation curves (Eq. (4)).

From the analysis of derived correlations for mass and energy yields, the temperature of 150 °C seems to show the lower temperature limit for components degradation reactions which occur during HTC of wood chips. Starting with this temperature, biomass components start to decompose; and with higher temperatures, hydrochar mass loss and heating value growth is intensifying. As a result of the simultaneous action of these two factors almost balancing each other, the energy yield reduces only slightly with temperature.

At the same time, the variations of the residence time and w/b ratio influence the hydrochar energy yield. Averaged over the temperature range, the energy yields for HTC-3h-6, HTC-6h-6, and HTC-3h-8 are 78%, 73%, and 75%, respectively. Similar tendencies are reported in literature [2, 19]. A higher amount of water in case of HTC-3h-8 resulted in hydrolysis reactions' intensification [2] in comparison with HTC-3h-6. The enhancement of decomposition reactions leads to a more significant mass loss and heating value increase, and the energy yield decreases, as a consequence. With regard to the reaction time influence, over the range of studied parameters, longer residence time resulted in a more complete carbonization of the feedstock material. Hydrochar samples HTC-6h-6 within all studied temperatures have the strongest effect on the mass yield decrease and growth of hydrochar energy content. Under these circumstances, the energy yield values for the residence time of six hours are the lowest among the investigated process parameter sets. Nevertheless, the influence of the residence time during HTC could become negligible in case of a sufficiently long treatment (as it was previously mentioned for the experiments by Román et al. [2]).

Table 2 summarizes the published results of HTC treatments at temperatures 210 – 230 °C for several biomass materials. The hydrothermally carbonized biomass mass yield varies from 36% to 71% of its original weight. Higher values correspond to wood species

(loblolly pine, Tahoe mix and beech) while processing of biomass residuals (such as walnut shell) indicated quite high levels of mass loss. Differences in conversion rates could be seen for energy yield as well: from 81% for deciduous beech to 50% for hydrochar from walnut shell. Even though the operational settings applied in presented experiments vary significantly, especially with respect to residence time (from 30 min to 20 hours) and mass ratio between water and biomass (from as low as 3% of biomass in the mixture to 20%), yields of hydrochar are mostly determined by biomass type.

**Table 2.** Mass and energy yields for different biomasses subjected to HTC treatment.

Feedstock material	T [°C]	t [h]	w/b ratio [-]	MY [-]	EY [-]	Reference
Coniferous wood chips	220	3	6:1	0.63	0.78	Current study
Loblolly pine	230	1.3	5:1	0.71	0.80	[9]
Tahoe mix	215	0.5	8:1	0.69	0.76	[5]
Beech	210	3	7:1	0.68	0.81	[28]
Bamboo	220	6	30:1	0.45	0.77	[6]
Walnut shell	230	20	20:1	0.36	0.50	[2]
Sugarcane bagasse	215	0.5	8:1	0.64	0.68	[5]

T: temperature; t: time; w/b ratio: water to biomass ratio; MY: mass yield; EY: energy yield.

## 4 Conclusions

Hydrothermal carbonization converts biomass into a value-added product with improved fuel properties. The process takes place in hot saturated water, and as a consequence, biomass with a high moisture content could be used as a feedstock without preliminary drying. Additionally, biomass components become less stable with the presence of water under saturated conditions, and the decomposition occurs more intensively. As a result, feedstock loses volatile compounds while the fixed carbon content significantly increases in the solid product. The resulting hydrochar is a more homogeneous and brittle material with the decreased ability of absorbing moisture.

The current work presents the results of hydrothermal carbonization of wood chips. Published experimental data on coniferous biomass HTC treatment is somewhat scarce, and the influence of the reaction temperature, residence time, and ratio between water and biomass on the energy densification and solid product yield was evaluated for the first time. The process temperature in the range of 180 – 250 °C significantly affects the process performance. The mass yield of hydrochar noticeably decreases with temperature: biomass loses on average 20% more mass at 250 °C than at 180 °C. The heating value of hydrochar can be increased by 36-40% at the highest temperature level. Within the investigated parameters, both the residence time and the mass ratio between water and biomass have a certain effect on the hydrochar yield and heating value. Higher carbonization rates are achieved with bigger quantities of water, as a consequence of hydrolysis reaction intensification. As a result of more complete biomass component decomposition, longer residence time leads to a higher mass loss and stronger increase of heating value of hydrochar. For all experimental sets, a

considerable decrease of mass yield with the reaction temperatures leads to slightly a descending character of energy yield with the intensification of carbonization: the values are varying from 78% to 73% on average.

In this study, the dependencies of mass and energy yields on the process parameters were expressed with mathematical correlations. The derived equations have a similar form with only the coefficients varying since both characteristics are naturally determined by the same process of carbonization. The obtained data could be applied for the process modelling, subsequent optimization, and integration with other processes.

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