

Examination of Torrefaction of *Leucaena Leucocephala* Under Pressure

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Abstract

In this study, the torrefaction of *Leucaena Leucocephala* at 200-250 °C under volumetric pressure up to 4 MPa was examined. It was found that the yield of solid product or torrefied leucaena increased with the increase in pressure. As large as 92.6 % of carbon was recovered in the torrefied leucaena prepared at 250 °C and 4 MPa. The higher heating value (HHV) of leucaena torrefied at high pressure increased significantly when compared to that of leucaena torrefied at atmospheric pressure. As large as 95 % of energy yield was achieved with the mass yield of 75 % for the torrefaction at 250 °C and 4 MPa. From the subsequent pyrolysis in TGA, leucaena torrefied under pressure showed the difference of weight decreasing curves comparing to that of leucaena torrefied at atmospheric pressure. The char yield at 800 °C for the leucaena torrefied at high pressure increased with the increase in pressure. These results suggested that the structure of leucaena was changed by the torrefaction under pressure and the cross-linking reactions during the subsequent pyrolysis were enhanced by the pressure resulting in increase in char yields.

Keywords: Biomass, Torrefaction, Pyrolysis, Upgrading

1. Introduction

Torrefaction is one of the thermal treatment techniques at relative low temperature range of 200-300 °C in an inert atmosphere, which aims to improve the fuel properties of biomass attractively for further utilization such as combustion, gasification and/or co-combustion. Several studies have been conducted on the properties of torrefied biomass including woody and non-woody biomass by varying temperature and holding time during torrefaction. It was found that the energy density as well as the higher heating value (HHV) was increased progressively at higher torrefaction temperature and at longer holding time [1]. As the previous studies showed, most of the studies were performed at atmospheric pressure in which although the biomass properties were found to improve significantly, the relatively low yield comparing to the gained calorific value of torrefied biomass tends to be the limitation. Thus, in order to solve these barriers, the torrefaction under pressure seems to be one of the challenge topics proposed. To date, few studies have been conducted to examine the effect of pressure on the biomass properties during pyrolysis.

In this study, the volumetric pressure has been applied during the torrefaction of woody biomass. The woody biomass used in this study was *Leucaena Leucocephala*. Leucaena has been

torrefied at low temperature at atmospheric pressure and under pressure up to 4 MPa in inert atmosphere. Throughout the torrefaction, properties of the torrefied leucaena were investigated.

2. Experimental

2.1 Material

Woody biomass (*Leucaena leucocephala*) was used as a sample in this study. It was first shredded with a cutting mill and ground with a ball mill in order to obtain a sample particle size less than 75 µm. Then, the sample was dried in vacuum oven at 70 °C for 24 h before the experiments.

2.2 Torrefaction experiment

Fig. 1 shows the schematic diagram of the torrefaction experimental unit used for this study. The reactor is made of stainless steel with the outside diameter of ½ in and 150 mm in length. The pressure transducer is connected at the top end of the reactor in order to monitor the change of pressure in real time during the experiment. On each run, fine sample of around 150 mg was placed in the 15 mm-length stainless steel reactor. The helium (99.999% purity) was then purged into the reactor in order to remove the air inside for several times. The furnace was then heated up to the desired temperature (200 °C, 225 °C and 250 °C) and held for 30 min. After reaching the

desired conditions, the reactor was placed in the middle of the furnace. For torrefaction under pressure, the desired pressure inside the reactor was controlled by the initial compressing of helium into the reactor at certain pressure values before starting the experiment. For torrefaction at atmospheric pressure, the valve at the top end was opened allowing the gas flow into the gas bag throughout the experiment.

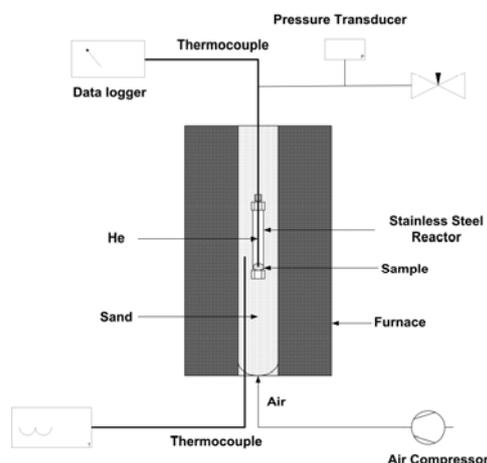


Fig.1 Schematic diagram of torrefaction under pressure

2.3 Evolved Gas Analyses by TG-MS technique

A quadrupole mass spectrometer (Perkin-Elmer, Clarus 500 MS) coupled to the thermobalance (Perkin-Elmer, Pyris1 TGA) was used for the evolved gas analysis during the pyrolysis. The pyrolysis experiments were performed at a heating rate of 10 °C/min up to the final temperature of 800 °C under the helium flow rate of 50 ml/min. To avoid secondary reactions, a probe was placed very close to the sample pan of the thermobalance in the direction of the gas flow. The transfer lines between the TGA and the MS were heated to 200 °C in order to avoid cold spots and thus prevent the condensation of the gaseous products. The signals for mass numbers of 2, 15, 18, 28, and 44 were continuously detected. Then the mass numbers were converted to the concentrations of H₂, CH₄, H₂O, CO, and CO₂ by referring to the calibration curves constructed using the standard gases. The evolving rates of the gaseous products were estimated from the measurements.

3. Results and Discussion

3.1 Product Yields and Carbon Distributions through the Torrefaction

It is well-known that the torrefaction temperature is very important parameter affecting the solid yield and their properties, then in this study, the solid yield was preliminarily investigated by varying temperature from 200-250 °C. Fig. 2 shows the solid yields of leucaena after torrefaction at various temperatures and pressures. It was found that the solid yield decreased with increasing torrefaction temperature. For example, the solid yields at atmospheric pressure were 88.2 %, 82.2 % and 73.9 % at 200 °C, 225 °C and 250 °C, respectively. With increasing pressure, the solid yields were found to increase gradually from atmospheric conditions. They, for example, increased from 88.2 % to 89.9 % during torrefaction at atmospheric pressure to 4 MPa for leucaena torrefied at 200 °C. On the other hand, at 225 °C and 250 °C, the solid yield was found to decrease when the pressure was increased to 1 MPa. However, it was found to increase by a few percentages later after the pressure was raised. These behaviors showed the strong effect of pressure by enhancing the decomposition of leucaena during the rising of pressure to 1 MPa at the temperature higher than 225 °C. However, at elevated pressure from 1 MPa to 4 MPa, the condensation of released volatile was promoted by the rising of pressure showing the continue increase in solid yield.

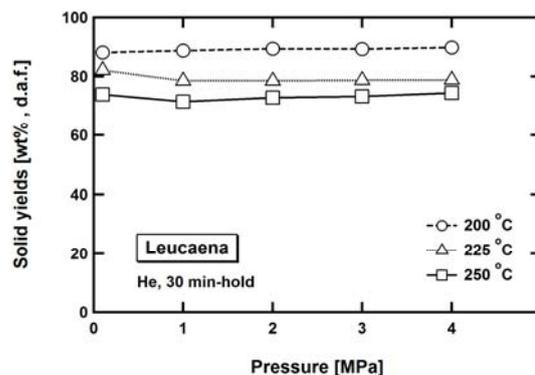


Fig.2 Solid yields obtained from torrefaction under pressure.

Fig. 3 shows the distributions of products through the torrefaction at various reaction temperatures and pressures. Around 0.7-9.0% CO₂ were also produced progressively with the increase in torrefaction temperatures and pressures. In this study, however, the measurement of H₂O was unavailable since its rapid condensation took place inside the reactor during rapid quenching of reactor in water. The amounts of H₂O and condensables were therefore

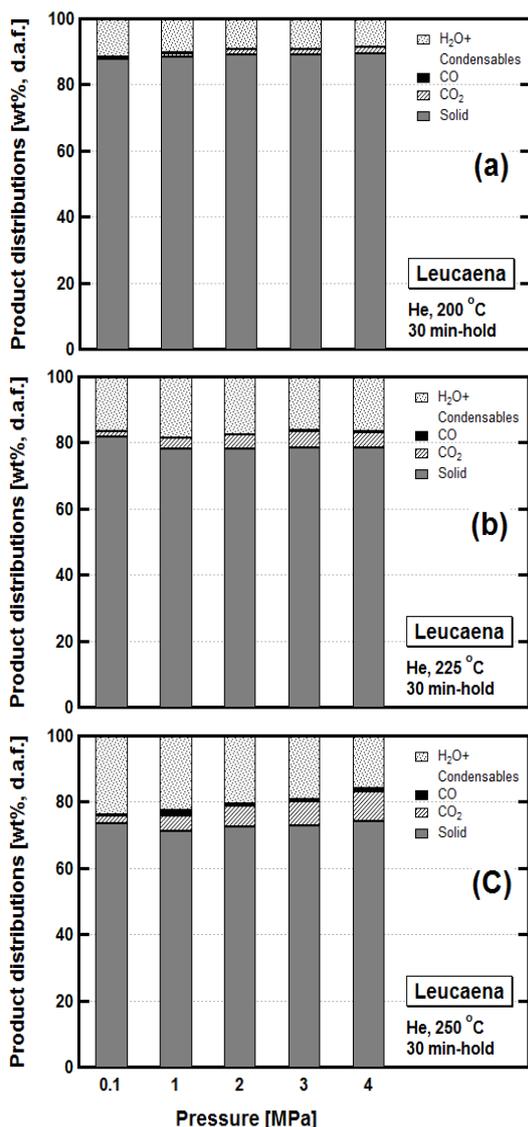


Fig. 3 Product distributions of leucaena torrefied under pressure at (a) 200 °C, (b) 225 °C and (c) 250 °C

shown together as the difference values from over all quantified products. However, since large amount of H₂O, which is mainly from hemicellulose decomposition [2], was produced during torrefaction and also increased with torrefaction temperatures, the distributions of carbon in the products were judged to be more informative. The distributions of carbon in the products were estimated from the yields of carbon contains in each products, and they are shown in Fig. 4. Now, the difference values became smaller and they can be considered as only carbon found in the condensables. From the experiments, it was found that around 79.6-93.7 % of carbon was recovered in the solid product. With the increase in torrefaction pressure, carbon in solid product was found to increase continuously while the carbon in

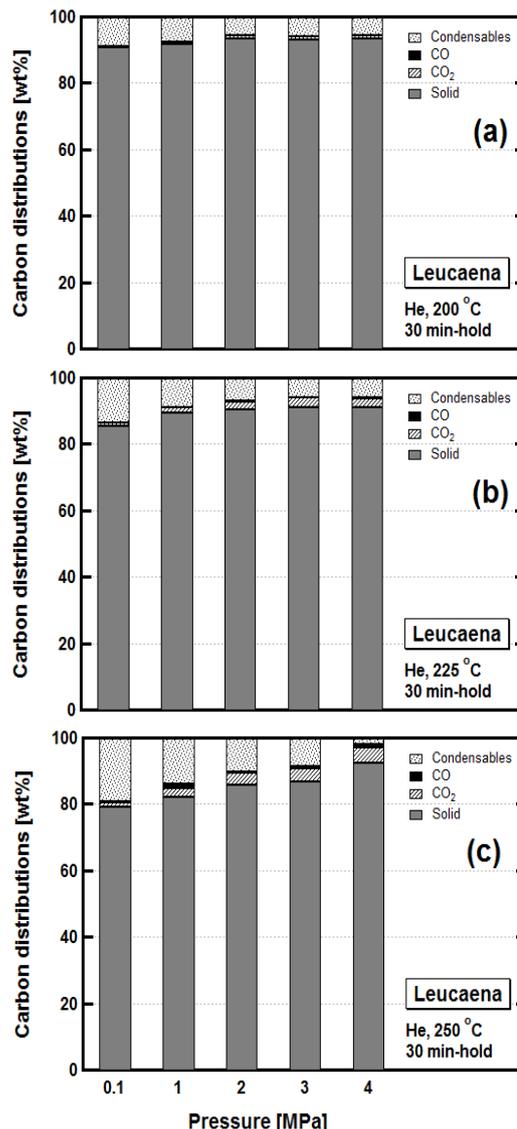


Fig. 4 Carbon distributions of leucaena throughout torrefaction under pressure at (a) 200 °C, (b) 225 °C and (c) 250 °C

condensables showed the opposite trend. For example, at 250 °C, carbon going to solid increased from 79.6 % to 82.4 %, 86.1 %, 87.2 % and 92.6 % for the torrefaction at atmospheric pressure, 1 MPa, 2 MPa, 3 MPa and 4 MPa, respectively. On the other hand, carbon going to condensables which was found large amount at atmospheric pressure (18.9 %) almost disappeared (1.8 % left) at torrefaction pressure of 4 MPa. In another word, the different product found from torrefaction at 250 °C, 4 MPa (Fig. 3) was almost H₂O. Therefore, it can be concluded that during torrefaction we can recovered the higher carbon by increasing the pressure.

3.2 Chemical Properties of Leucaena Torrefied under Pressure

Table 1 Ultimate analysis and the higher heating value (HHV) of leucaena and torrefied leucaena

Sample	Ultimate analyses [wt%, d.a.f.]				HHV	Yield
	C	H	N	O (diff)	[MJ/kg]	[wt%, d.b.]
Leucaena	50.1	7.4	0.7	41.8	20.4	-
<i>condition [°C-MPa]</i>						
200-0.1	51.7	7.4	0.7	40.2	21.2	88.2
200-1	52.0	7.5	0.7	39.8	21.4	88.8
200-2	52.5	7.5	0.7	39.3	21.6	89.4
200-3	52.4	7.5	0.7	39.4	21.6	89.3
200-4	52.2	7.4	0.7	39.7	21.4	89.9
225-0.1	52.4	7.4	0.7	39.5	21.5	82.2
225-1	57.2	6.4	0.8	35.6	23.6	78.6
225-2	57.9	6.5	0.8	34.8	24	78.6
225-3	58.2	6.6	0.8	34.4	24.2	78.8
225-4	58.1	6.5	0.8	34.6	24.1	78.9
250-0.1	54.0	6.4	0.7	38.9	21.9	73.9
250-1	57.7	5.7	0.9	35.7	23.4	71.5
250-2	59.2	5.8	0.9	34.1	24.3	72.9
250-3	59.6	5.6	0.9	33.9	24.3	73.3
250-4	62.3	5.6	1.0	31.1	25.8	74.4

Table 1 shows the ultimate analyses of raw and torrefied leucaena preparing at elevated temperatures and pressures. In this study, the higher heating value (HHV) was obtained by using Friedl *et al.*'s formula [3] as follows:

$$HHV \text{ (MJ/kg)} = 5.22C^2 - 319C - 1647H + 38.6CH + 133N + 21,028 \quad (1)$$

where C represents percentage of carbon content, H represents percentage of hydrogen content and N represents nitrogen content in the structure determined on a dry-ash-free basis. As Table 1 shows, the carbon content was found to increase significantly with the increase in torrefaction temperatures and pressures. For the hydrogen content, approximately 1 % decrease was observed while the nitrogen content did not change much with the increase in torrefaction temperatures. The oxygen content appeared to decrease significantly with the increase in torrefaction temperature, and the decreasing of the oxygen content seemed to be more pronounced when prepared at higher pressures: the oxygen content was found to decrease from 38.9 % to 31.1 % of atmospheric pressure to 4 MPa at 250 °C, respectively. These resulted in the increase in HHV of torrefied leucaena with the increase in torrefaction temperature and

pressure. The increase in torrefaction pressure did not affect much the nitrogen content in the torrefied leucaena. It was noted that the HHV of leucaena increased as large as 17.8 % when the pressure increased from atmospheric to 4 MPa at torrefaction temperature of 250 °C.

Next, in order to examine the fuel properties of torrefied leucaena, the elemental composition of leucaena as well as leucaena torrefied at various conditions were also plotted on H/C vs. O/C diagram as shown in Fig. 5.

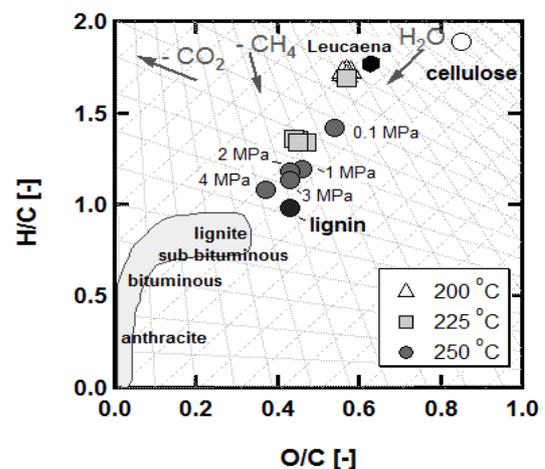


Fig. 5 H/C and O/C diagram of leucaena and leucaena torrefied under pressure

From Fig. 5 raw leucaena was plotted at H/C = 1.77 and O/C = 0.63 while the torrefied leucaena were plotted at lower value ratios, lying along the dehydration reaction line (- H₂O). The H/C and O/C values of torrefied leucaena, for example, move from H/C = 1.42 and O/C = 0.54 to H/C = 1.08 and O/C = 0.37 when the torrefaction pressure increased from atmospheric to 4 MPa at 250 °C, respectively. This indicated that the torrefaction of leucaena proceeded through the coalification process resulted in the values of H/C and O/C very close to lignite. The position of H/C and O/C values also showed that the leucaena torrefied under high pressure gave the better elemental fuel properties than that of leucaena torrefied at atmospheric pressure.

3.3 Thermal Analyses

As the results in the previous section showed, since the elemental properties of torrefied leucaena was found attractive from the torrefaction at 250 °C, thus the analyses hereafter will focus on this torrefaction temperature. The thermal analyses include the pyrolysis behaviors performing in nitrogen atmosphere by using TG-MS technique. The combustion behaviors of leucaena torrefied under pressure were also examined in air by using TGA.

3.3.1 Pyrolysis Behaviors of Leucaena Torrefied under Pressure

Fig. 6 shows the weight decreasing curves of raw and torrefied leucaena prepared at 250 °C by varying torrefaction pressure, during heating to 800 °C at a heating rate of 10 °C/min in flow of nitrogen. In order to compare with the raw leucaena, the weight of the torrefied leucaena was normalized by multiply the weight with the yield of the torrefied leucaena. From the

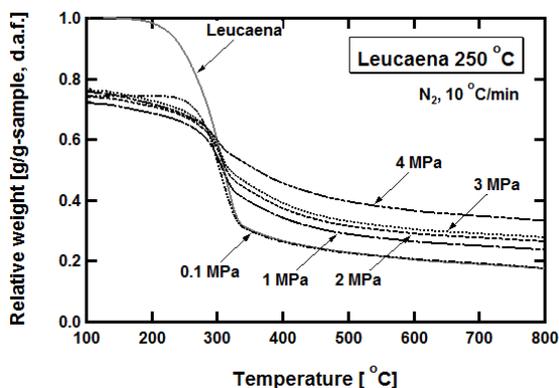


Fig. 6 Weight decreasing curves of leucaena and leucaena torrefied under pressure at 250 °C

experiments, the significant difference of weight decreasing profiles among raw leucaena, leucaena torrefied at atmospheric pressure and leucaena torrefied at elevated pressure was observed. The weight of raw leucaena started to decrease around 150 °C and decreased rapidly at around 250-320 °C. After that, the weight decreased gradually when increasing the temperature to 800 °C. The weight of leucaena torrefied at atmospheric pressure started to decrease at the temperature higher than 200 °C, which was very close to that of final torrefaction temperature, then decreased rapidly at around 250-320 °C. On the other hand, the weight of leucaena torrefied at high pressure (1-4 MPa) showed the different behaviors. The weight of leucaena torrefied at high pressure started to decrease at temperature lower than 200 °C and decreased rapidly at around 250-400 °C. After that, the weight decreased gradually when increasing the temperature to 800 °C. Moreover, it was found that the char yield at 800 °C for the leucaena torrefied at high pressure was higher than the char yield of raw leucaena and the leucaena torrefied at atmospheric pressure. The char yield at 800 °C for the leucaena torrefied at atmospheric pressure was almost the same as that of the raw leucaena. On the other hand, the char yield at 800 °C for the leucaena torrefied at high pressure increased with the increase in torrefaction pressure: the char yield increased from 17.5% to 33.2 % when increasing the pressure from 1 MPa to 4 MPa. The increase in char yield could be explained by the progress of the cross-linking reactions occurred during the pyrolysis. More discussion will be shown in the next section. These results suggested that the structure of leucaena was changed by the torrefaction under pressure and the cross-linking reactions during the pyrolysis were enhanced by the pressure during the torrefaction resulting in increase in char yields.

3.3.2 Product Distributions and Gas formation Rates through the Subsequent Pyrolysis of Leucaena Torrefied under Pressure

Next, the product distributions throughout the pyrolysis at 600 °C for raw leucaena and leucaena torrefied at 250 °C under pressure were investigated as shown in Fig. 7. The product distributions of the torrefied leucaena were normalized with the solid yield obtaining from the torrefaction for each studied conditions. It was found that the char yield of the raw leucaena and the leucaena torrefied at

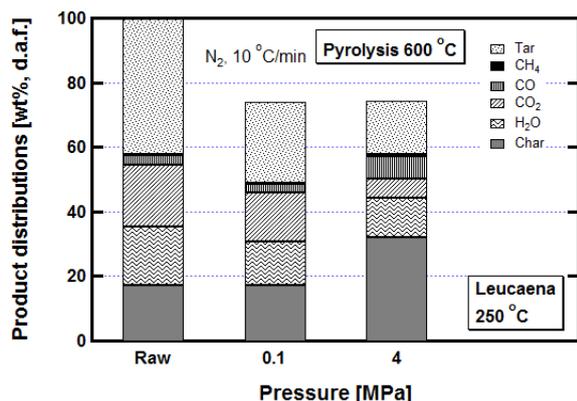


Fig. 7 Product distribution throughout the pyrolysis at 600 °C for raw leucaena and leucaena torrefied under various pressures at 250 °C

atmospheric pressure were almost the same. On the other hand, the char yield significantly increased with the increase in pressure during the torrefaction. The yield of CO₂ decreased significantly with the increase in pressure during torrefaction: it decreased from 15.2 % to 5.8 % when increased the torrefaction pressure from atmospheric pressure to 4 MPa. The yield of CO increased with the increase in torrefaction pressure: it increased from 2.6 % to 7.0 % when increased the torrefaction pressure from atmospheric pressure to 4 MPa. H₂O was found to decrease progressively with the increase in torrefaction pressure: it decreased from 18.4 % to 13.6 % and 12.1 % for raw leucaena, leucaena torrefied at atmospheric pressure and leucaena torrefied at 4 MPa, respectively. In addition, the significant reduction of tar with the increasing of pressure was also observed. The tar yield reduced from 41.9 % for the pyrolysis of the raw leucaena to 25.1 % and 16.5 %, for leucaena torrefied at atmospheric pressure and 4 MPa, respectively. These results were judged to be due to the enhancing of cross-linking reactions by the torrefaction under pressure as discussed in section 3.3.1.

4. Conclusions

In this study, the upgrading of leucaena by torrefaction under pressure at 0.1-4 MP and vary the temperature from 200-250 °C was examined. During the torrefaction, the yield of torrefied leucaena was found to decrease with the increase in torrefaction temperature, whereas the yield of torrefied leucaena increased with the increase in torrefaction pressure. From the elemental analyses, the higher carbon content in torrefied leucaena can be achieved by the rising

of torrefaction pressure. As large as 92.6 % of carbon was recovered in the torrefied leucaena prepared at 250 °C and 4 MPa. While the oxygen content decreased to 31.1 % for the torrefied leucaena prepared at 250 °C and 4 MPa. The higher heating value (HHV) increased significantly when compared to that of torrefied at atmospheric pressure. As large as 94.3 % of energy yield was achieved with the mass yield of 74.4 % for the torrefaction at 250 °C and 4 MPa. From the subsequent pyrolysis and combustion in TGA, leucaena torrefied under pressure showed the difference of weight decreasing curves comparing to that of torrefied at atmospheric pressure. It was found that the weight of leucaena torrefied at high pressure started to decrease at temperature lower than 200 °C. The char yield at 800 °C for the leucaena torrefied at high pressure increased with the increase in torrefaction pressure. These results suggested that the structure of leucaena was changed by the torrefaction under pressure and the cross-linking reactions during the pyrolysis were enhanced by the pressure during the torrefaction resulting in increase in char yields. The substantial increase in char combustion rate was also found for leucaena torrefied under pressure. These results showed that the leucaena could be upgraded efficiently by the torrefaction under pressure at 1-4 MPa.

5. Acknowledgement

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6. References

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