

Kinetic Scheme to Predict Product Composition of Biomass Torrefaction

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A kinetic scheme for the prediction of product composition of torrefaction is presented in this work. The scheme is based on a pyrolysis scheme for fast pyrolysis of small ash free biomass particles and was adapted to consider the presence of secondary char formation reactions, the inhibition of sugar formation due to the catalytic effect of alkali metals in biomass, as well as the typical hemicellulose structure of hardwoods. The torrgas composition predicted by the model is compared to experimental data of torrefaction in a lab-scale packed bed reactor. It is shown that the adapted model is able to predict the yields of the main volatile groups, i.e., permanent gases, light and heavy condensable species and the yields of the several groups in which condensable species were classified based on their structure, i.e., carbonyls and alcohols, furans, phenolics as well as water vapour.

1. Introduction

Torrefaction is a mild pyrolysis process at temperatures ranging from 220 to 350 °C, in which mainly the hemicellulose fraction is decomposed. Biomass loses mass and gets enriched in carbon due to volatiles release. Additionally, torrefaction improves grindability, prolongs durability, increases hydrophobicity and reduces biological and thermal degradation, which improves shelf life, storage and transportation. Due to these benefits interest in torrefaction has grown in the recent years.

Most of the current pyrolysis and torrefaction mechanisms are not able to predict the composition of the products of the process, therefore a model which is able to predict product composition in these processes is required. The kinetic scheme presented in this work to model biomass torrefaction is based on the scheme developed by Ranzi et al. (2008) for fast pyrolysis of small ash free biomass particles, i.e., primary pyrolysis. In this scheme biomass consists of cellulose, hemicellulose and 3 types of lignin which independently decompose. The volatiles are represented by 20 species, including main permanent gases and condensable species.

This scheme was already applied to describe biomass torrefaction by the authors of this paper in Mehrabian et al. (2013). It was shown that the scheme was able to model the mass evolution of micro-TGA experiments of torrefaction. It was also applied to predict the product composition of torrefaction experiments in a lab-scale reactor. The solid and total volatile yields were correctly predicted, but there were large deviations in the predictions of some of the volatile species, as water vapour, acetic acid or sugars (levoglucosan and xylosal).

An adaptation of the original scheme is proposed in this work to include the presence of secondary char formation reactions, which are relevant for particles of a certain thickness, as under typical torrefaction or pyrolysis conditions. In these reactions char is produced together with other products, as H₂O and CO₂, from the original products of primary pyrolysis. Moreover, in the competition between fragmentation and sugar formation reactions, the catalytic effect of alkali metals in biomass, together with the presence of secondary reactions of the volatiles in particles of a certain thickness, leads to the preference of the fragmentation pathway over sugar formation for both cellulose and hemicellulose (Mamleev et al., 2009).

This adapted scheme is applied in this work to biomass torrefaction and the predictions of the model are compared with experimental data to check the validity of the adaptation.

2. Kinetic scheme

The original scheme developed by the group of Ranzi is summarized in Figure 1 (Ranzi et al, 2008). Cellulose can be converted to active cellulose without appreciable mass loss through R1 or converted to char and water through R4, being reaction R1 the prevalent reaction in this competition. When active cellulose is formed, it is almost instantaneously consumed (at low or medium heating rates, < 20 K/s) either through the ring fragmentation (R2) or the transglycosylation (R3) pathways. The adaptation of the scheme is summarized in Figure 1 and the reactions are shown in Table 1. Cellulose pyrolysis is described with just one reaction representing devolatilization plus an inclusion of a secondary reaction representing charring. The kinetics of this devolatilization reaction are the kinetics of the reaction to produce active cellulose (R1) in the original scheme. But this reaction would directly produce the fragmentation products (previous R2), and no LVG (previous R3). An adjustable parameter “ x_1 ” represents the amount of the initial fragmentation primary products – (Vol.+Char)_{1,1}, including several low molecular weight compounds as hydroxyacetaldehyde (HAA), CO₂ or H₂O – that react to form the secondary products – (Vol.+Char)_{2,1} –. In the secondary charring reaction, producing (Vol.+Char)_{2,1}, not just H₂O is produced together with char, but also CO₂ and H₂.

The hemicellulose scheme is based on pyrolysis of xylan, which is a good representative of the hemicelluloses of hardwoods. It consists of two successive reactions, resembling the first one the cellulose scheme. The adaptation of the scheme is made following the same principles as for the adaptation of the cellulose scheme. The competition between R6 and R7 is eliminated and just the fragmentation pathway is followed, producing (Vol.+Char)_{5,1} directly from R5. The secondary charring products, produced from the previous fragmentation products, are considered through the parameter “ x_6 ”. In the decomposition of HCA2, through R8, the presence of secondary reactions are also considered through the parameter “ x_8 ”. Acetic acid is also included in the initial composition of hemicellulose. The main hemicellulose macromolecule of hardwoods is acetylglucuronoxylan, composed of 10 xylose molecules, 7 acetyl groups and 1 glucuronic acid. The acetyl groups represent around 15 % of the mass. In the original scheme hemicellulose is represented by xylan (C₅H₈O₄). In the adapted scheme hemicellulose will be represented by 10 of the previous xylan molecules (C₅H₈O₄) per 4 acetic acid (C₂H₄O₂, AA in Table 1 and Figure 1) ones, so that the acetic acid molecules represent around 15 % of the initial mass. The CHO content of the new representative hemicellulose molecule is almost not affected. The acetic acid will be released with the first hemicellulose reaction (R5). This adaptation is just representative for hemicelluloses of hardwoods, as it is based on a typical hemicellulose hardwood molecule.

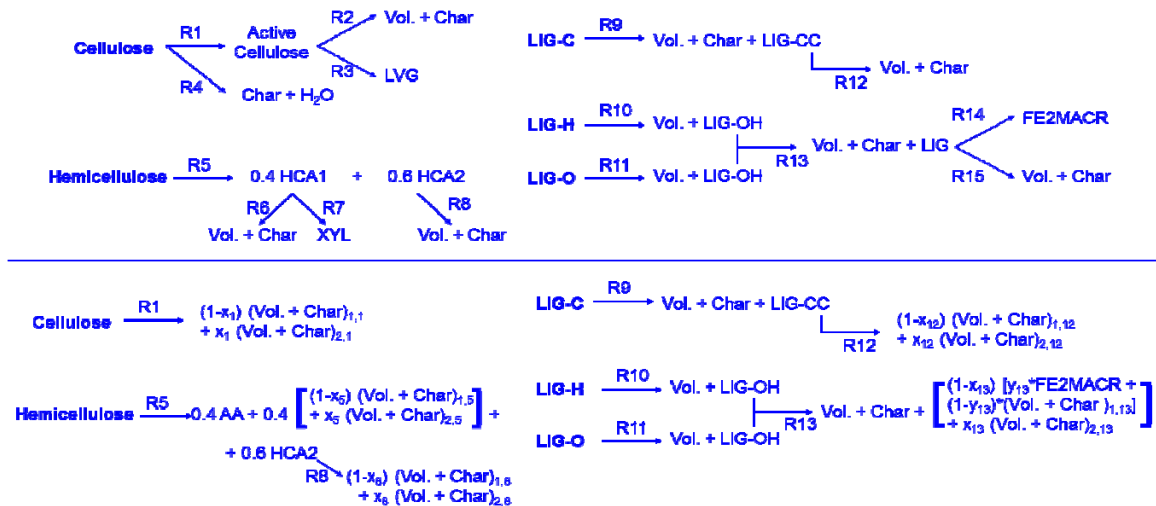


Figure 1: Original scheme from Ranzi et al. (2008) (top) and adapted scheme (bottom)

The original scheme of lignin consists of three different components: LIG-C, LIG-H and LIG-O, which are richer in carbon, hydrogen and oxygen, respectively. The modifications are done in the decomposition of LIG-OH and LIG-CC to include secondary charring reactions. As in the case of cellulose and hemicellulose, in the adapted scheme the mass loss evolution is not altered for heating rates lower than 20 K/s. Just the final char yield and product composition are different. In this scheme char is not just

produced as pure carbon, but also as several G{} forms (G{CO₂}, G{CO}, G{COH₂}) and G{H₂}) that further react at higher temperatures producing CO₂, CO or H₂, but these reactions are not active at typical torrefaction temperatures. The adjustable parameters “x_i” representing the amount of secondary charring reactions were set equal to 0.3 for all reactions in the adaptation of the scheme.

Table 1: List of reactions of the adapted scheme

		Reaction	A [s ⁻¹]	E [kJ/mol]
1	CELL	→ (1-x ₁) * (0.95 HAA + 0.25 GLYOX + 0.2 CH ₃ CHO + 0.25 HMFU + 0.2 C ₃ H ₆ O + 0.16 CO ₂ + 0.23 CO + 0.9 H ₂ O + 0.1 CH ₄ + 0.61 Char) + x ₁ * (5.5 Char + 4 H ₂ O + 0.5 CO ₂ + H ₂)	8 × 10 ¹³	192.5
5	HCE	→ 4/10 AA + 0.4 * [(1-x ₅) * (0.75 G{H ₂ } + 0.8 CO ₂ + 1.4 CO + 0.5 CH ₂ O + 0.25 CH ₃ OH + 0.125 ETOH + 0.125 H ₂ O + 0.625 CH ₄ + 0.25 C ₂ H ₄ + 0.675 Char) + x ₅ * (4.5 Char + 3 H ₂ O + 0.5 CO ₂ + H ₂)] + 0.6 HCEA2	1 × 10 ¹⁰	129.7
8	HCEA2	→ (1-x ₈) * (0.2 CO ₂ + 0.5 CH ₄ + 0.25 C ₂ H ₄ + 0.8 G{CO ₂ } + 0.8 G{COH ₂ } + 0.7 CH ₂ O + 0.25 CH ₃ OH + 0.125 ETOH + 0.125 H ₂ O + Char) + x ₈ * (4.5 Char + 3 H ₂ O + 0.5 CO ₂ + H ₂)	1 × 10 ¹⁰	138.1
9	LIG-C	→ 0.35 LIG-CC + 0.1 pCOUMARYL + 0.08 PHENOL + 0.41 C ₂ H ₄ + H ₂ O + 0.495 CH ₄ + 0.32 CO + G{COH ₂ } + 5.735 Char	4 × 10 ¹⁵	202.9
10	LIG-H	→ LIG-OH + C ₃ H ₆ O	2 × 10 ¹³	156.9
11	LIG-O	→ LIG-OH + CO ₂	1 × 10 ⁹	106.7
12	LIG-CC	→ (1-x ₁₂) * (0.3 pCOUMARYL + 0.2 PHENOL + 0.35 C ₃ H ₄ O ₂ + 0.7 H ₂ O + 0.65 CH ₄ + 0.6 C ₂ H ₄ + G{COH ₂ } + 0.8 G{CO} + 6.4 Char) + x ₁₂ * (14.5 Char + 3 H ₂ O + 0.5 CO ₂ + 4 H ₂)	5 × 10 ⁶	131.8
13	LIG-OH	→ H ₂ O + CH ₃ OH + 0.45 CH ₄ + 0.2C ₂ H ₄ + 1.4 G{CO} + 0.6 G{COH ₂ } + 0.1 G{H ₂ } + 4.15 Char + [(1-x ₁₃) * (y ₁₃ * FE2MACR + (1 - y ₁₃) * (H ₂ O + 0.5 CO + 0.2 CH ₂ O + 0.4 CH ₃ OH + 0.2 CH ₃ CHO + 0.2 C ₃ H ₆ O + 0.6 CH ₄ + 0.65 C ₂ H ₄ + G{CO} + 0.5 G{COH ₂ } + 5.5 Char)) + x ₁₃ * (10.5 Char + 3 H ₂ O + 0.5 CO ₂ + 3 H ₂)] y ₁₃ = - 3.680E-11 * T ⁵ + 8.262E-08 * T ⁴ - 6.891E-05 * T ³ + 2.613E-02 * T ² - 4.591 * T + 4.041E+02; T in [°C]	3 × 10 ⁸	125.5
16	G{CO ₂ }	→ CO ₂	1 × 10 ⁵	100.4
17	G{CO}	→ CO	1 × 10 ¹³	209.2
18	G{COH ₂ }	→ CO + H ₂	5 × 10 ¹¹	272.0
19	G{H ₂ }	→ H ₂	5 × 10 ¹¹	313.8

3. Experimental setup

The lab-scale reactor is a discontinuously operated pot furnace. It consists of a cylindrical retort (height 0.35 m, i.d. 0.12 m), heated electrically by two separated PID controlled-heating circuits. The biomass is put into a cylindrical holder (0.100 m height and 0.095 m i.d.) which is located inside the cylindrical retort. Nitrogen is introduced through a porous plate at the bottom of the fuel bed to keep the system inert and to remove the volatiles. Torrefaction of beech woodchips at 250 °C and 285 °C temperatures has been investigated with the lab-scale reactor as described in Mehrabian et al. (2013). A filled pot with beech woodchips of 2-2.5 cm and a moisture content of 6.4 wt.% results in a fuel bed of about 10 cm height and 190 g biomass. Temperatures were measured with thermocouples at different heights inside the bed. The torrgas is extracted from above the fuel bed and introduced to the FT-IR to measure the concentrations of the permanent gases and light condensable species listed in Table 2. H₂ was additionally measured by a heat capacity method. In addition, the tar content of the torrgas was measured using a gravimetric method as well as by gas chromatography (GC) coupled to mass spectrometry (MS) to identify the compounds and a flame ionization detector (FID) to quantify them. The 130 detected compounds by GC-MS-FID were classified based on the structure in 3 different groups: phenolic, cyclic (as furfural) and not cyclic (as hydroxyacetone). One sugar compound, levoglucosan, was also detected.

Table 2: Experimental and model product composition in mass percentage of initial wet biomass

	Beech 250 °C				Beech 285 °C			
	<i>Exper.</i>	<i>Original scheme</i>	<i>Adptd. scheme</i>	<i>Prins /Bates</i>	<i>Exper.</i>	<i>Original scheme</i>	<i>Adptd. scheme</i>	<i>Prins /Bates</i>
Total solid	71.682	74.47	74.94	77.92	58.008	62.22	64.02	66.15
Hydrogen	0.145	0.00	0.09		0.118	0.00	0.14	
Carbon monoxide	1.009	0.70	1.39	0.44	1.650	1.01	1.80	0.63
Carbon dioxide	4.937	2.04	3.25	2.14	6.457	2.70	4.37	3.07
Methane	0.132	0.68	0.70		0.406	1.04	1.00	
Ethylene	0.012	0.58	0.56		0.004	0.90	0.78	
Propane	0.011				0.027			
Propene	0.294				0.561			
Total permanent gas	6.54	3.99	5.98	2.57	9.22	5.65	8.10	3.70
Formaldehyde	0.284	1.21	1.05		0.322	1.83	1.43	
Acetaldehyde	0.015	0.00	0.12		0.058	0.01	0.37	
Propanal (Acetone)	0.002	1.04	1.19		0.006	1.18	1.65	
Methanol	0.527	0.95	0.92	2.07	0.860	1.48	1.35	4.38
Ethanol	1.252	0.36	0.34		1.973	0.54	0.45	
Hydroxyacetaldehyde / Acetic acid	4.221	0.01	3.52	2.42	6.081	0.05	5.54	4.21
Water vapour	12.463	6.99	9.21	11.64	16.152	7.71	11.81	14.55
Glyoxal		0.00	0.20			0.01	0.61	
Propanedial		0.00	0.00			0.00	0.00	
Lactic acid	0.271			1.85	0.394			4.14
Formic acid	0.005			0.89	0.037			1.60
Total light condensable species	19.04	10.57	16.55	18.87	25.88	12.82	23.21	28.87
Levogluconan		3.13				9.53		
Xylose monomer		4.91				5.09		
p-Coumaryl		0.08	0.08			0.13	0.13	
Phenol		0.04	0.04			0.07	0.07	
Sinapaldehyde		2.80	1.98			4.46	3.15	
HMFU		0.01	0.43			0.03	1.32	
Furfural				0.11				0.16
Hydroxyacetone				0.52				1.11
Gravimetric tar	2.739				6.888			
Total heavy condensable species	2.74	10.97	2.53	0.64	6.89	19.32	4.66	1.27

4. Results and discussion

The original and adapted kinetic schemes are applied to describe the experiments as explained in Mehrabian et al. (2013), dividing the fuel bed into three layers along the height of the bed and modelling separately the evolution of each layer by the kinetic model. The entire fuel bed mass loss profile and the final product composition are obtained by a mass weighted average of the results of these three layers.

The final product compositions obtained experimentally and by the original and adapted mechanism are summarized in Table 2. The predictions of the two step kinetic model mechanism developed by Prins et al. (2006) from experiments with willow (hardwood), including the products of each reaction proposed by Bates and Ghoniem (2012), is also included for comparison. The several detected and predicted volatiles species are classified in three different groups: permanent gas, light condensable species and heavy condensable species. The mass of initial humidity of biomass is included as water vapour in the model predictions, together with the vapour released during torrefaction of the dry biomass. Permanent gas includes species as H₂, CO, CO₂ and light hydrocarbons. The light condensable species include several oxygenated species that can be detected by FT-IR. The boiling points of these species are between -19 °C

of formaldehyde or 21 °C of acetaldehyde to 118, 122 and 131 °C of acetic acid, lactic acid and hydroxyacetaldehyde, respectively. The heavy condensable species are measured experimentally by the gravimetric method and some components are detected by GC-MS-FID. In the models, species as hydroxyacetone and furfural, with boiling points of 146 °C and 162 °C, respectively, are considered as heavy condensable species. These species were detected by GC, so they are present in the gravimetric tar fraction. The other components from the models included as heavy condensable species have boiling points higher than 160 °C.

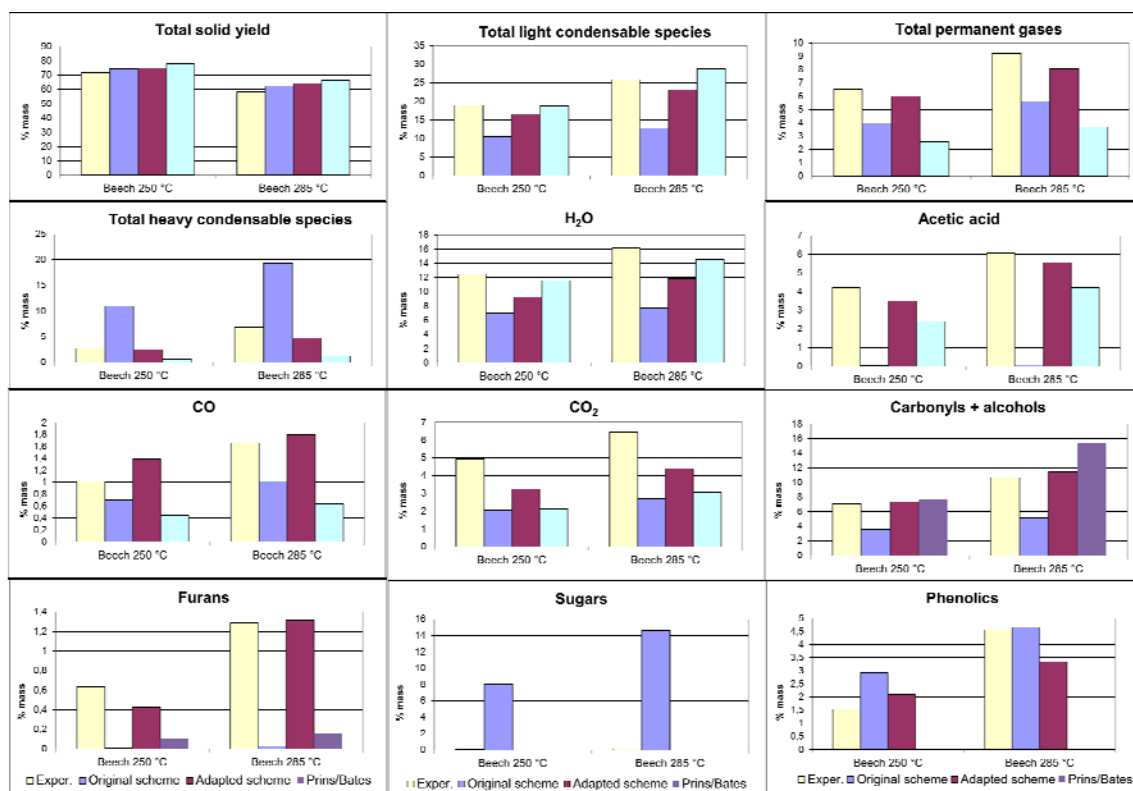


Figure 2: Product composition of the main groups and species in mass percentage of initial wet biomass

The final solid yield is reasonably well predicted by all schemes, although the time evolution (not shown) is not precisely described due to the simplified description of the reactor. The yields of total permanent gas, light and heavy condensable species are correctly predicted by the adapted scheme. The original scheme predicts very high yields of sugars as levoglucosan or xylose, which leads to a strong over-prediction of the total heavy condensable species. On the other hand, the light condensable species and permanent gas are underpredicted by the original scheme. The Prins/Bates scheme shows an under-prediction of the total permanent gases and heavy condensable species. A different comparison is shown in Table 3, where the condensable species are classified in four main groups, according to the structure of the compounds, and water vapour. The light condensable species, with the exception of water vapour, are included in the group of “carbonyls+alcohols”. The gravimetric tars identified by GC-MS-FID are included in different groups. The aromatic compounds belong to the phenolics group, the cyclic aliphatic compounds (as furfural) are included in the group furans and the not cyclic compounds (as hydroxyacetone) in the group “carbonyls+alcohols”. A sugar, levoglucosan, was also detected. The not GC identified fraction of the gravimetric tars is assumed to be pyrolytic lignin (Scholze and Meier, 2001) and included in the phenolics groups. The adapted scheme shows again a good prediction for the yields of the different groups. The original scheme extremely over-predicts the yields of sugars, which are present in very low amounts, and under-predicts the yields of furans and carbonyls+alcohols. The Prins/Bates scheme underpredicts the yields of some groups as furans or phenolics. In Figure 2 the yields of the several groups and some of the main components are also shown. The adapted scheme has an accurate prediction of the yield of acetic acid due to the inclusion of the production of acetic acid from hemicellulose. The yields of CO are slightly over-predicted and the yields of CO₂ slightly under-predicted, but the predictions of the adapted scheme are more accurate than the original or the Prins/Bates schemes. The water vapour yield is under-predicted by the adapted scheme. The prediction of the Prins/Bates scheme is in this case better.

Table 3: Product composition of the main groups in mass percentage of initial wet biomass (w.t.%)

	Beech 250 °C				Beech 285 °C			
	Exper.	Original scheme	Adptd. scheme	Prins /Bates	Exper.	Original scheme	Adptd. schme	Prins /Bates
FTIR detected	6.576	3.573	7.339	7.233	9.730	5.108	11.408	14.327
Hydroxyacetone				0.522				1.111
Exp. GC detected	0.513				0.938			
Total carbonyls + alcohols	7.09	3.57	7.34	7.76	10.67	5.11	11.41	15.44
Furfural				0.114				0.163
HMFU		0.005	0.430			0.027	1.318	
Exp. GC detected	0.639				1.288			
Total furans	0.64	0.01	0.43	0.11	1.29	0.03	1.32	0.16
Levoglucozan	0.061	3.130			0.098	9.534		
Xylose monomer		4.914				5.095		
Total sugars	0.06	8.04	0.00	0.00	0.10	14.63	0.00	0.00
p-Coumaryl		0.079	0.079			0.130	0.130	
Phenol		0.040	0.040			0.065	0.065	
Sinapaldehyde		2.803	1.977			4.465	3.146	
Exp. GC detected	0.915				1.796			
Exp. not GC detected	0.611				2.768			
Total phenolics	1.53	2.92	2.10	0.00	4.56	4.66	3.34	0.00

5. Conclusions

In this work a kinetic scheme for the prediction of product composition and mass loss evolution of torrefaction is presented. The scheme is based on a pyrolysis scheme for fast pyrolysis of small ash free biomass particles and has been adapted to consider the presence of secondary char formation reactions, which are relevant for particles of a certain thickness, and the preference of the fragmentation pathway over sugar formation for both cellulose and hemicellulose, due to the catalytic effect of alkali metals in biomass, as well as the presence of acetyl groups linked to xylan in typical hemicelluloses of hardwoods. The torrgas composition predicted by the adapted model has been compared to experimental data of torrefaction in a lab-scale packed bed reactor. It is shown that the adapted model is able to correctly predict the yields of the main volatile groups, i.e., permanent gases (including CO₂ and CO), light and heavy condensable species; as well as the yields of the several groups in which the condensable species are classified. On the other hand, the original scheme and another scheme from the literature show large deviations for some groups.

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