SUPPORTING INFORMATION

Alkali Lignin Stabilization of Oil-in-Water Emulsions via Simple Dispersion and Ozonation Processes

*Maëva Peloille,[a] Frédérique Ham-Pichavant,[a] Marie Reulier,[b] Cécile Joseph,[b] Henri Cramail,[a]**

*Stéphane Grelier[a]**

[a] Université de Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600 Pessac, France

[b] ITERG, 11 rue Gaspard Monge, 33610 Canéjan, France

Pages: 13

Figures: 5

Tables: 3

Scheme: 1

TABLE OF CONTENTS

- **Lignin characterization and ozonation optimization**

Figure S1: Schematic representation of the ozonation reaction setup

Figure S2: ^{31}P NMR spectra of AL, Hydr-AL (after drying) and Ozon-AL with chemical shifts corresponding to OH groups

Table S1: Lignin ozonation optimization conditions and results

Figure S3: Molar masses distributions for AL, Hydr-AL and the ozonated lignins obtained in the different conditions described in **Table S1**

Scheme S1: Detailed proposed mechanism for the effect of ozone on lignin phenol groups through **a)** heterolytic cleavage (acidic conditions) and **b)** homolytic cleavage

Table S2: Particle sizes and zeta potential values for aqueous dispersion of Hydr-AL and Ozon-AL

- **Emulsion characterization**

Table S3: Droplet size and polydispersity (PDI) values of O/W (20:80 w/w) emulsions prepared from Hydr-AL and Ozon-AL

Figure S4: Transmittance profiles for O/W (20:80 w/w) emulsions prepared from **a)** Hydr-AL, **b)** Ozon-AL, and **c)** LS, taken during analytical centrifugation (800 g, 30 min, 25 °C).

Figure S5: Transmittance profiles for O/W (20:80 w/w) emulsions prepared from Ozon-AL at pH12, taken during analytical centrifugation (800 g, 30 min, 25 °C) (left) and associated optical microscopy images (right)

- **Lignin characterization and ozonation optimization**

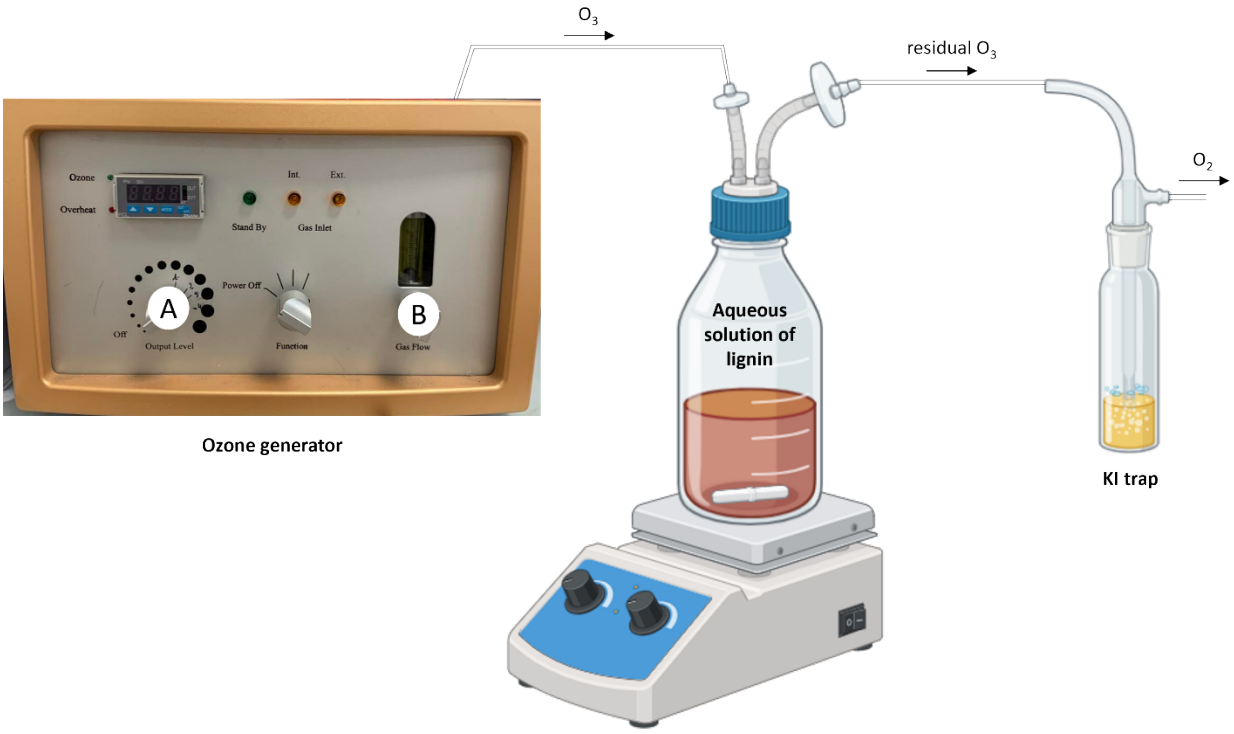


Figure S1: Schematic representation of the ozonation reaction setup

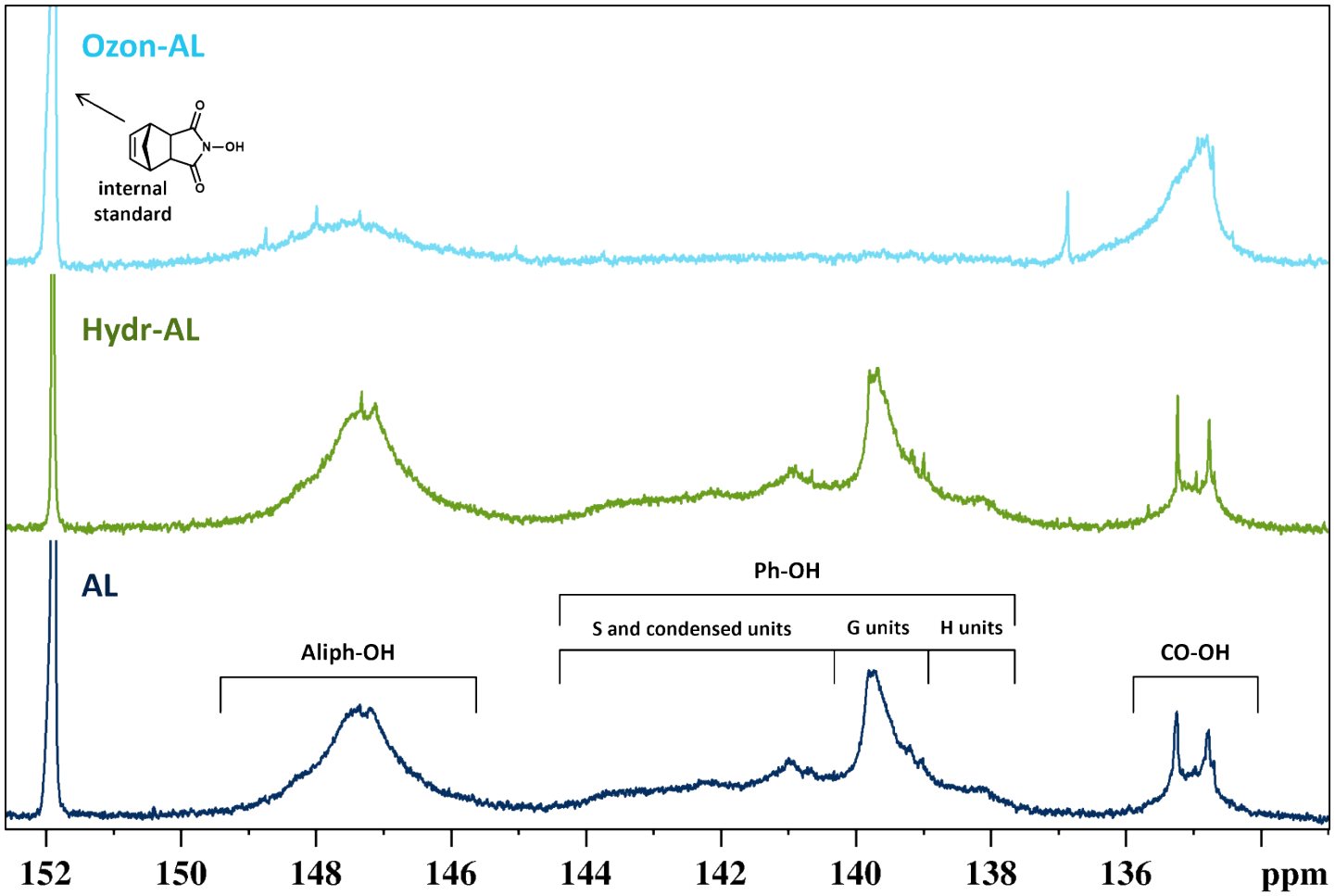


Figure S2: ^{31}P NMR spectra of AL, Hydr-AL (after drying) and Ozon-AL with chemical shifts corresponding to OH groups

Table S1: Lignin ozonation optimization conditions and results

Entry	Hydr-AL concentration	Time (min)	Electric field power	Ozone release	Mass yield	Solution pH	Water solubility	OH groups quantification (mmol/g)			M_w (g/mol)	Đ
								Aliph-OH	Ph-OH	CO-OH		
AL	-	-	-	-	-	-	-	1.62	2.51	0.48	18500	7.7
Hydr-AL	-	-	-	-	-	3.5 ± 0.0	-	1.62 ± 0.08	2.54 ± 0.09	0.42 ± 0.02	18800	9.8
1	10 wt%	240	Medium	Diffusion at the surface	99.5 ± 3.5%	3.2 ± 0.0	27.5 ± 7.8%	1.28 ± 0.02	0.97 ± 0.08	0.86 ± 0.01	12300	8.2
2	1 wt%	30	Maximum	Diffusion at the surface	103.3 ± 2.9%	2.8 ± 0.0	74.0 ± 17.4%	1.11 ± 0.07	0.72 ± 0.21	0.83 ± 0.09	8100	5.5
3	1 wt%	10	Maximum	Bubbling into the solution	105.0 ± 8.5%	2.7 ± 0.2	85.0 ± 2.8%	0.98 ± 0.05	0.18 ± 0.02	1.23 ± 0.19	4100	3.6

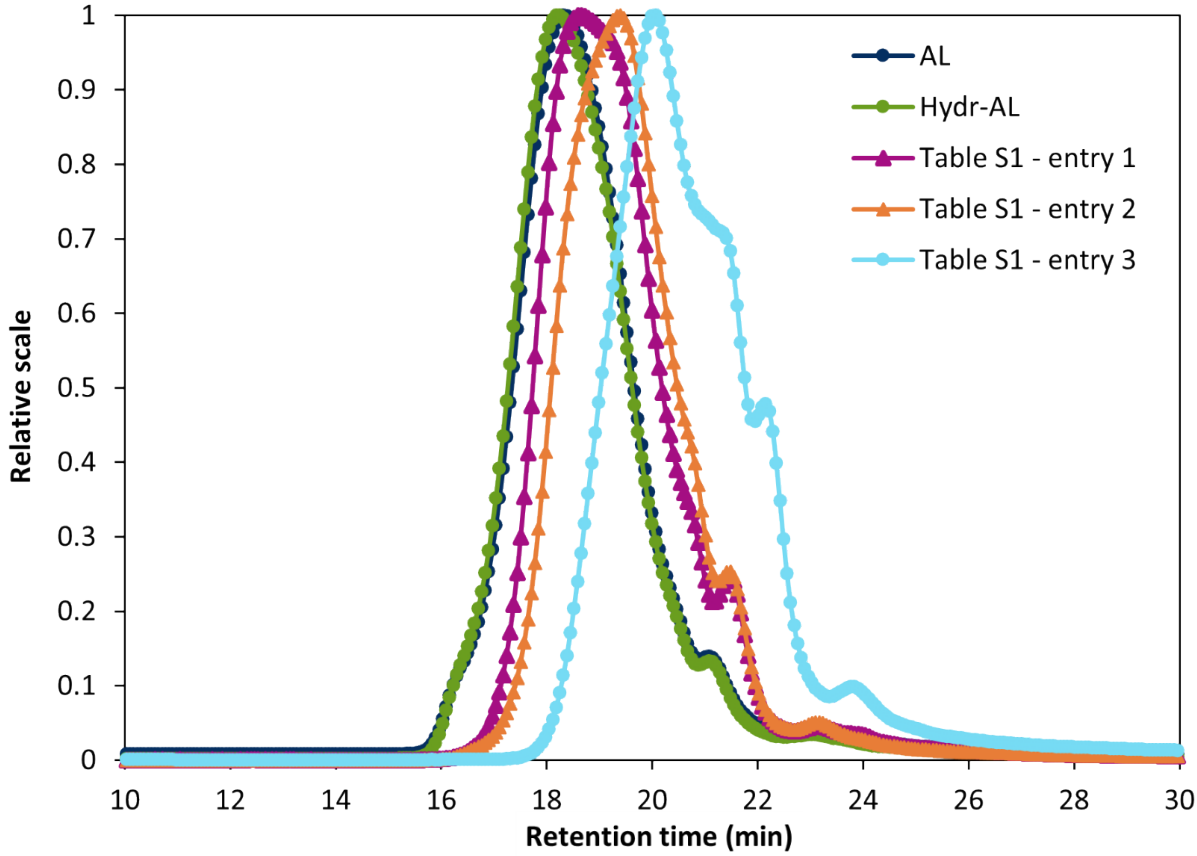


Figure S3: Molar masses distributions for AL, Hydr-AL and the ozonated lignins obtained in the different conditions described in **Table S1**

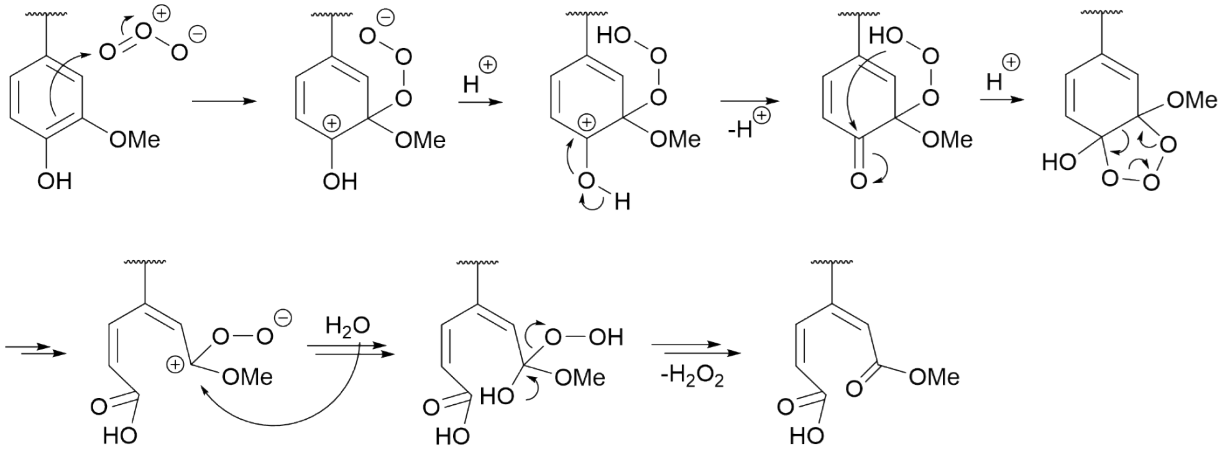
Ozonation reactions were performed on Hydr-AL solutions using the setup illustrated in **Figure S1** and optimized based on the results in **Table S1**. All the experiments were carried out at least in duplicate. Ozone was generated with a corona discharge generator, with several adjustable parameters, including:

- The power of the electric field producing ozone (button A in **Figure S1**), set either to an intermediate value ("Medium" in **Table S1**) or the maximum value ("Maximum" in **Table S1**)
- The method of ozone introduction into the system, either diffusing the gas at the solution surface or bubbling it directly into the solution, as indicated in **Table S1**
- The lignin solution concentration
- The reaction duration
- The oxygen source for ozone generation (O_2 bottle in all cases)
- The gas flow rate (button B in **Figure S1**) which was set to 5 mL/min in any case.

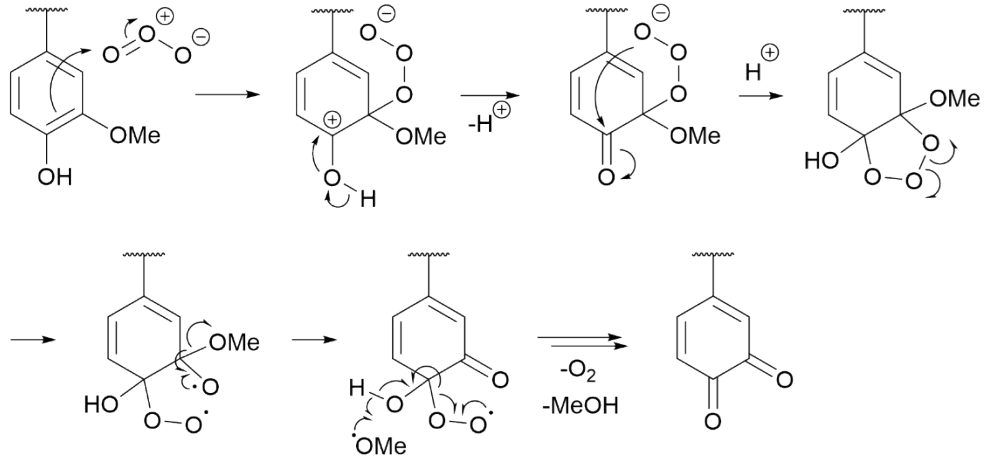
All reactions resulted in high mass yields. However, the conditions used in **Table S1- entry 1** were considered insufficient to enhance the hydrophilicity of Hydr-AL with low increase in carboxylic acid contents, minor decreases in phenolic content and molar masses **(Figure S3)** and subsequent low solubility in water after freeze-drying. The electric field power was increased, and the lignin concentration decreased to enhance ozone production, reduce the amount of lignin to be oxidized, and ultimately improve the reaction efficiency **(Table S1 – entry 2)**. These conditions allowed a reduction in the reaction time and resulted in a further decrease in phenolic content. However, no significant improvement in the carboxylic acid content was observed. SEC analysis revealed a slight reduction in molar masses compared to the previous conditions **(Figure**

S3). These results led to an improvement in water solubility, but the reproducibility was considered insufficient due to the high degree of uncertainty associated with water solubility. For all these reasons, we selected the conditions described in **Table S1 – entry 3**, which resulted in the most efficient lignin ozonation by simply bubbling the gas into the lignin solution rather than diffusing it on the surface of the solution. The resulting lignin was then used in the emulsion stabilization experiments presented in this study.

a) Heterolytic cleavage



b) Homolytic cleavage



Scheme S1: Detailed proposed mechanism for the effect of ozone on lignin phenol groups through **a)** heterolytic cleavage (acidic conditions) and **b)** homolytic cleavage

Table S2: Particle sizes and zeta potential values for aqueous dispersions of Hydr-AL and Ozon-AL

	Zeta potential (mV)	**Particle sizes (nm)**	
Hydr-AL	-57.0 ± 4.5	31.1 ± 2.2	226.7 ± 7.1
Ozon-AL	-37.6 ± 0.3	34.17 ± 3.0	243.5 ± 19.4

- **Emulsion characterization:**

Table S3: Droplet size and polydispersity (PDI) values of O/W (20:80 w/w) emulsions prepared from Hydr-AL and Ozon-AL

	Mean size $D_{3,2}$ (µm)	**Mean size $D_{4,3}$ (µm)**	**PDI**
Hydr-AL	8.6 ± 0.0	31.7 ± 0.2	0.702
Ozon-AL	13.9 ± 0.1	50.7 ± 0.3	0.455

Mean sizes $D_{3,2}$ (Sauter diameter) and $D_{4,3}$ (De-Brouckere or volumetric diameter) are defined as:

$$D_{3,2} = \frac{\sum_i n_i D_i^3}{\sum_i n_i D_i^2}$$

$$D_{4,3} = \frac{\sum_i n_i D_i^4}{\sum_i n_i D_i^3}$$

with n_i the number of droplets of diameter D_i.

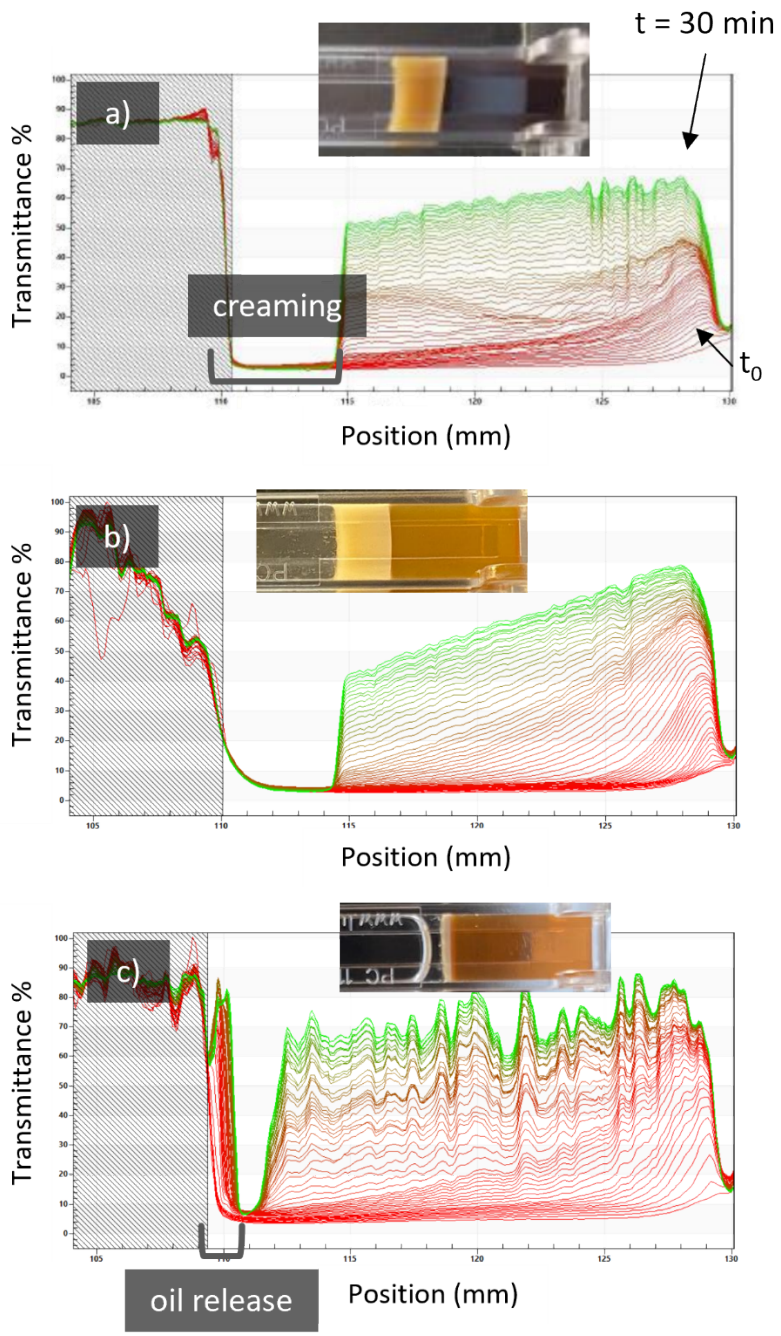


Figure S4: Transmittance profiles for O/W (20:80 w/w) emulsions prepared from **a)** Hydr-AL, **b)** Ozon-AL, and **c)** LS, taken during analytical centrifugation (800 g, 30 min, 25 °C).

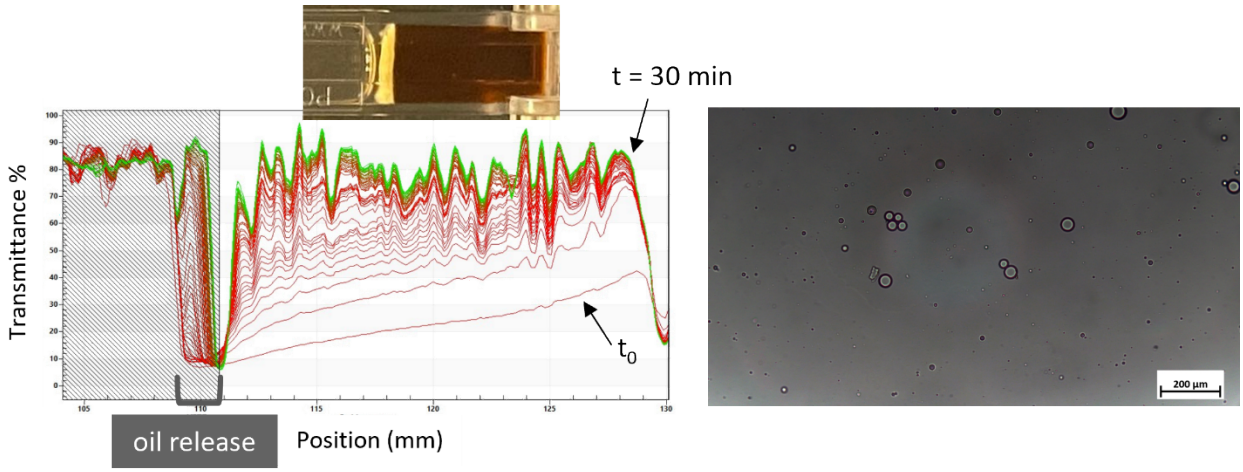


Figure S5: Transmittance profiles for O/W (20:80 w/w) emulsions prepared from Ozon-AL at pH 12, taken during analytical centrifugation (800 g, 30 min, 25 °C) (left) and associated optical microscopy images (right)