MULTI GRAM SCALE SYNTHESIS OF HMF AND COMPARATIVE ENVIRONMENTAL EVALUATION

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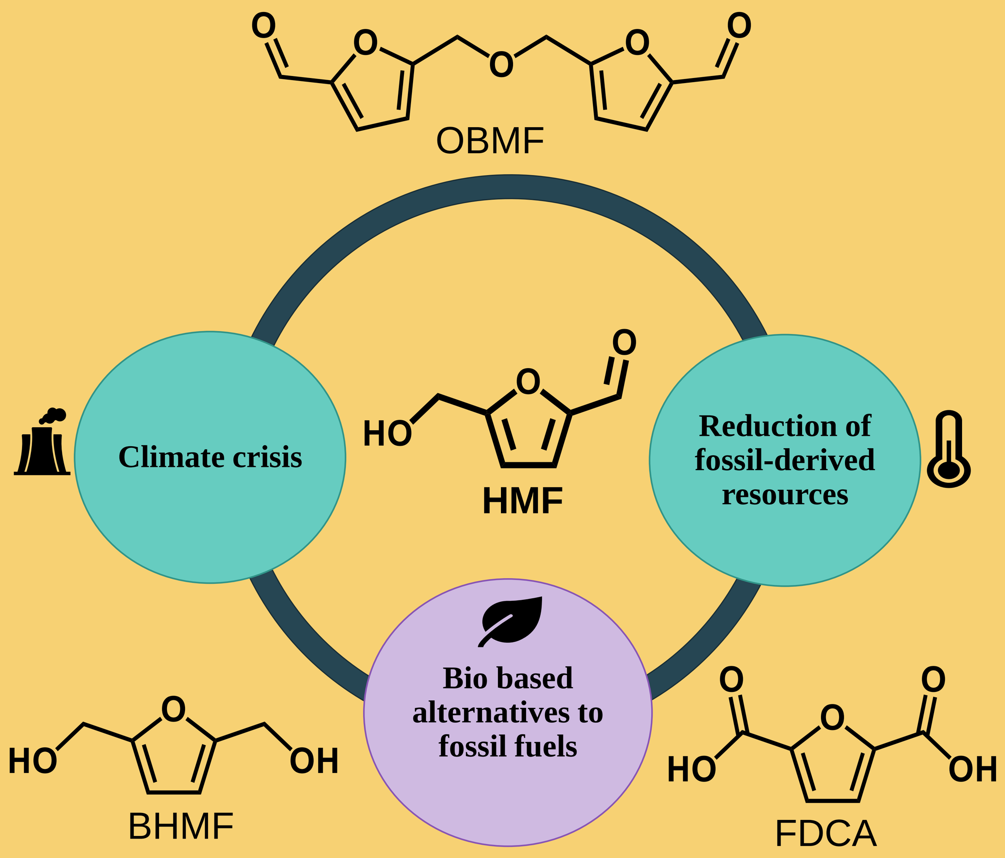
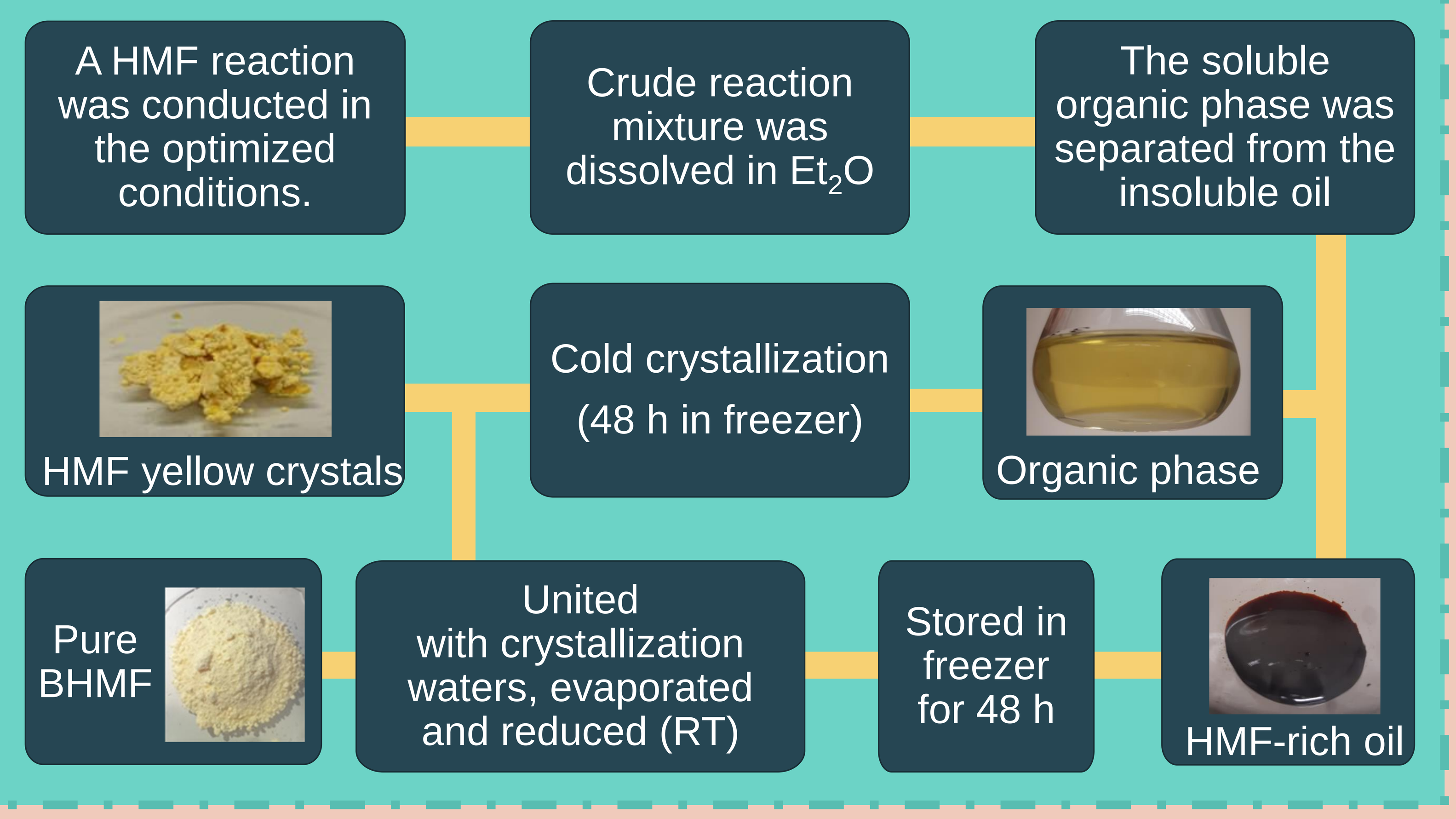
INTRODUCTION

Among the various molecules derived from renewables **HMF** is the one our studies focus on. Rapid advances are being made in enhancing HMF synthesis, but its industrialization is far from happening due to unresolved issues related to its isolation and stability.[1,2] Therefore, our goal was to develop an effective, green, high-yielding large-scale procedure for the synthesis and isolation of HMF, but also to boost HMF upgrading in other industrially appealing derivates.[3]

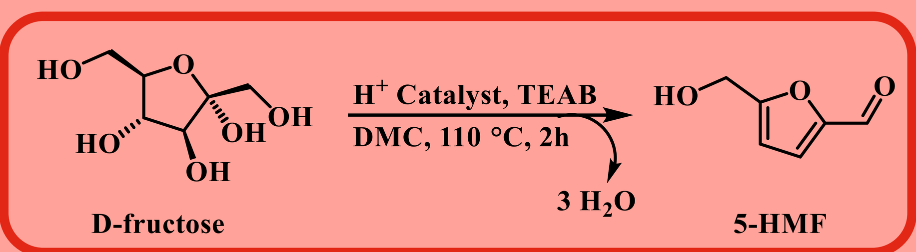


METHODOLOGY



RESULTS AND DISCUSSION

❖ Optimization of HMF synthesis



Catalyst optimization

Table 1. Optimization of the heterogeneous acidic catalyst.[a]

#	Acidic catalyst	Selectivity %[b] HMF	OBMF	Yield %[b]
1	Amberlyst-15	98	2	64
2	Amberlyst-36	98	2	65
3	Purolite CT151	94	6	66
4	Purolite CT269	97	3	67
5	Purolite CT275	96	4	63
6	**Purolite CT275DR**	**98**	**2**	**73**

Amount of TEAB

Table 3- Optimization of the amount of TEAB.[a]

#	DMC mL	TEAB % wt.	[H+] % wt.	t h	Selectivity[b] % HMF	OBMF	Yield[b] %
1	80	20	5	2	100	0	70
2	**80**	**10**	**5**	**2**	**100**	**0**	**70**
3	80	5	5	2	95	5	66
4	80	2	5	2	95	5	58
5	80	---	5	2	94	6	55

Reaction time optimization

Table 2- Optimization of reaction time[a]

#	DMC mL	TEAB % wt.	[H+] % wt.	t h	Sel.[b] % HMF	OBMF	Yield[b] %
1	80	20	10	1	91	9	68
2	**80**	**20**	**10**	**2**	**98**	**2**	**73**
3	80	20	10	3	94	6	75

Amount of Catalyst

Table 4- Optimization of the amount of catalyst.[a]

#	DMC mL	TEAB % wt.	[H+] % wt.	t h	Selectivity[b] % HMF	OBMF	Yield[b] %
1	80	20	10	2	98	2	73
2	**80**	**20**	**5**	**2**	**100**	**0**	**70**
3	80	20	2.5	2	100	0	53

Temperature optimization

Higher reaction temperatures (150 ºC) produced similar or worse HMF selectivity and yield. Several by-products started to appear because of side reactions and product degradation.

[a] Reaction conditions: 10 g of D-fructose dissolved in DMC/TEAB in presence of Purolite CT275DR, at 110 °C in autoclave; [b] Estimated via ^{1}H-NMR spectrum.

Amount of DMC

Table 5- Optimization of the amount of DMC.[a]

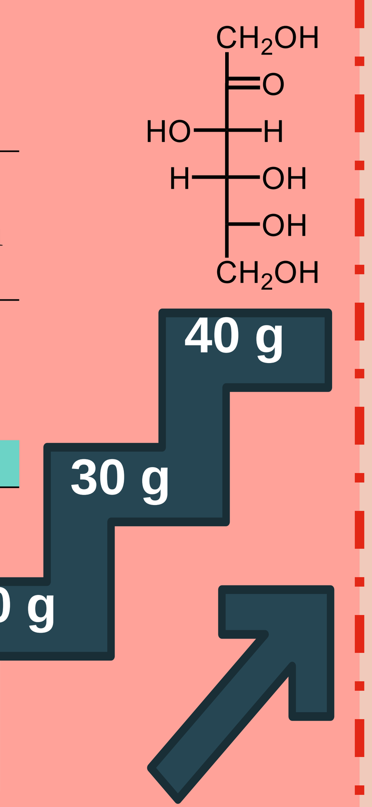
#	DMC mL	TEAB % wt.	[H+] % wt.	t h	Selectivity[b] % HMF	OBMF	Yield[b] %
1	80	10	5	2	100	0	70
2	50	10	5	2	98	2	70
3	**40**	**10**	**5**	**2**	**98**	**2**	**73**

❖ Scale-up

Table 7- Scale up HMF reactions in autoclave.[a1]

D-fruct. g	DMC mL	Crude HMF g	Selectivity %[b1] HMF	OBMF	HMF yield %[b1]	HMF crystals yield %	HMF-rich oil g	BHMF yield %[c1]	Total yield [d1]
10	40	5.37	98	2	73	47	1.86	75 (18)	65
20	80	11.21	98	2	76	44	4.61	78 (21)	65
30	120	17.08	97	2	77	45	6.72	70 (19)	64
40	**160**	**22.76**	**96**	**4**	**72**	**46**	**7.92**	**73 (17)**	**63**

[a1] Reaction conditions: D-fructose was dissolved in DMC/TEAB in the presence of Purolite CT275DR (5% wt.) at 110 °C in autoclave for 2h; [b1] Via ^{1}H-NMR spectroscopy; [c1] Isolated yield calculated with respect to the HMF contained in the residual oil; in parenthesis, yield calculated with respect to the starting amount of D-fructose; [d1] Considered as HMF crystals + HMF converted into BHMF.



❖ Comparison with previous work

Table 8- Comparison between the procedure reported in our previous work and in this work.

#	Method[a]	DMC mL	TEAB % wt.	Catalyst % wt.	T °C	t h	Yield % Oil	Cryst.	Rxn scale[b]
Prev.[4]	Reflux	80	20	Amb-15 (10)	90	16	70	/	20 g
This	Autoclave	40	10	CT275DR (5)	110	2	73	47	40 g

[a] Data refer to a D-fructose 10-gram scale procedure; [b] Maximum amount of D-fructose used.

❖ Green Metrics evaluation and Ecoscale algorithm

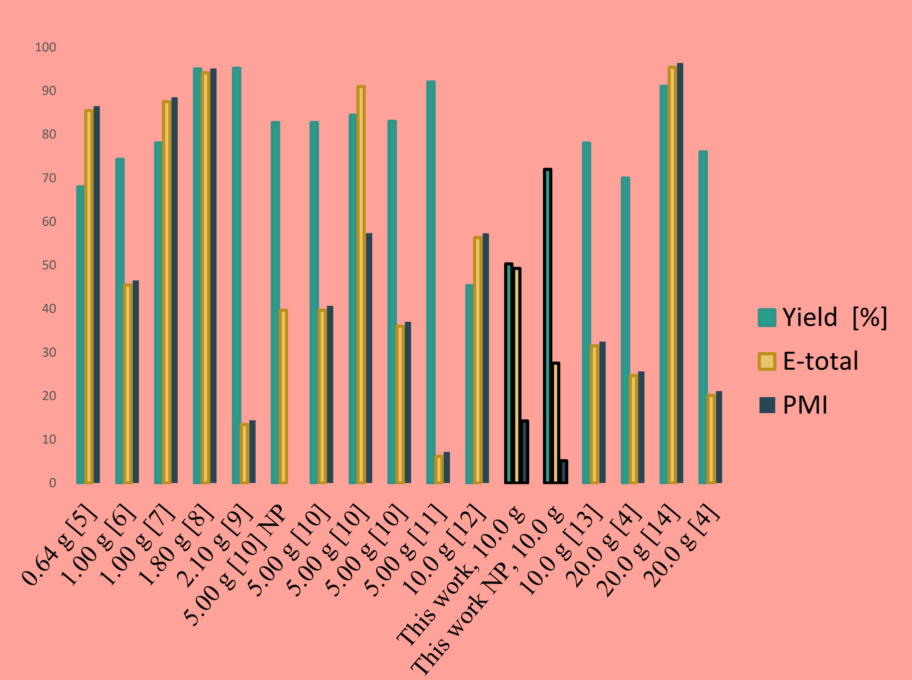


Figure 1. PMI, E-total and Yield values for different reported HMF synthesis (with PMI lower than 100) and ours; NP means that purification is not included in the calculations.

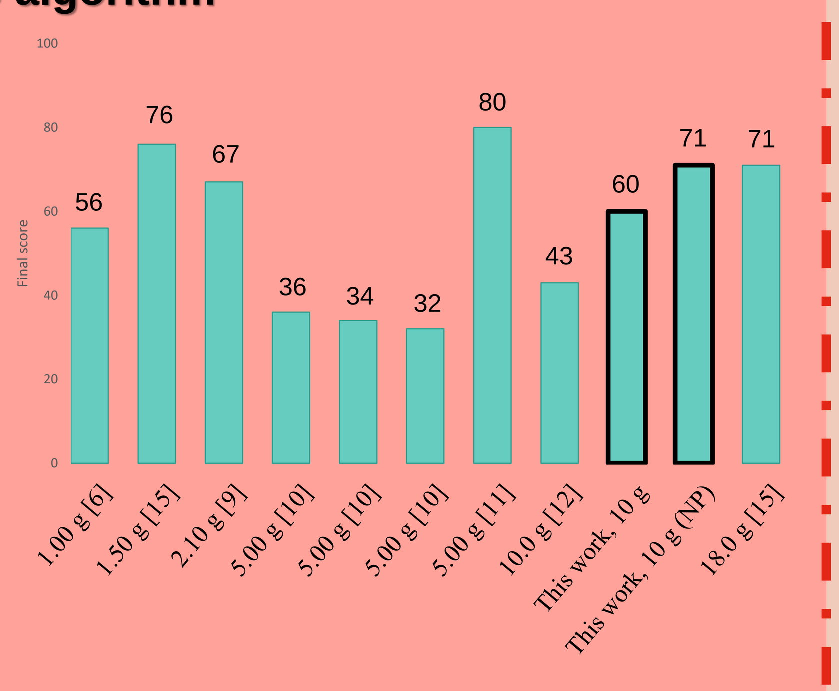
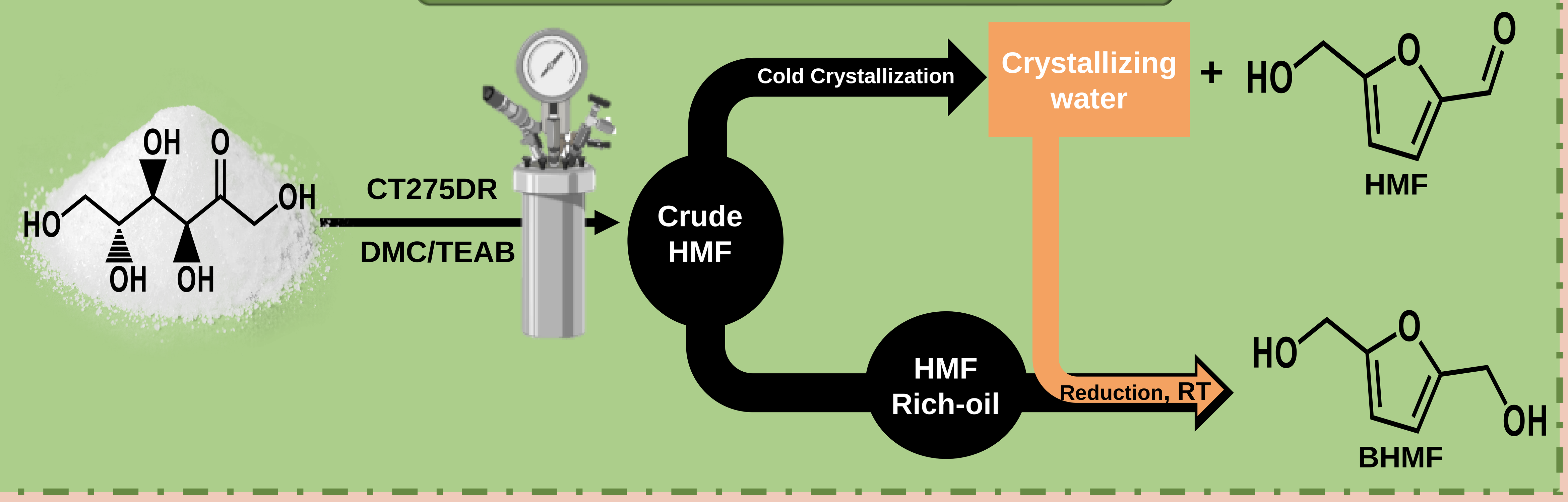


Figure 2. Ecoscale values for different reported HMF synthesis and ours. NP means that purification is not included in the calculations.

MULTI-GRAM SYNTHESIS



CONCLUSION

- Development of a fast, highly selective, efficient synthesis of HMF in autoclave;
- Custom-made purification that led to pure HMF and pure BHMF;
- Scale-up trials up to 40 g of starting material;
- Assessment of the ecological character of our procedure using green metrics and eco-scale;
- Many improvements compared to our previously developed procedure.

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