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Setting the gram scale synthesis of BHMF as a building block for new polymers production

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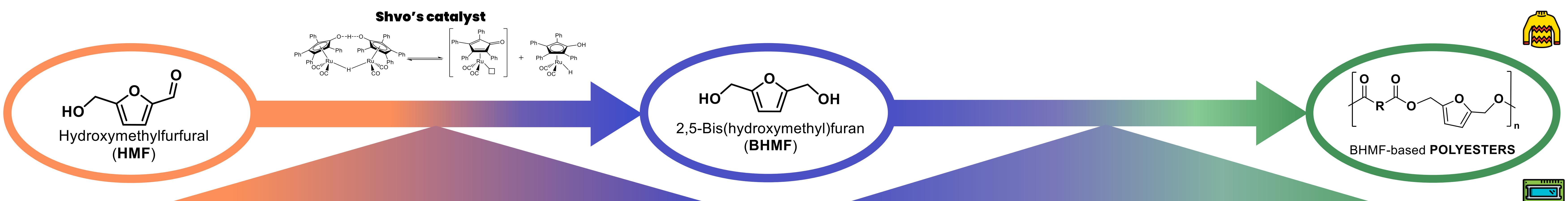
SPOKE, WP and TASKS

Spoke 8 **WP** 8.1 **Tasks** 8.1.1 & 8.1.3

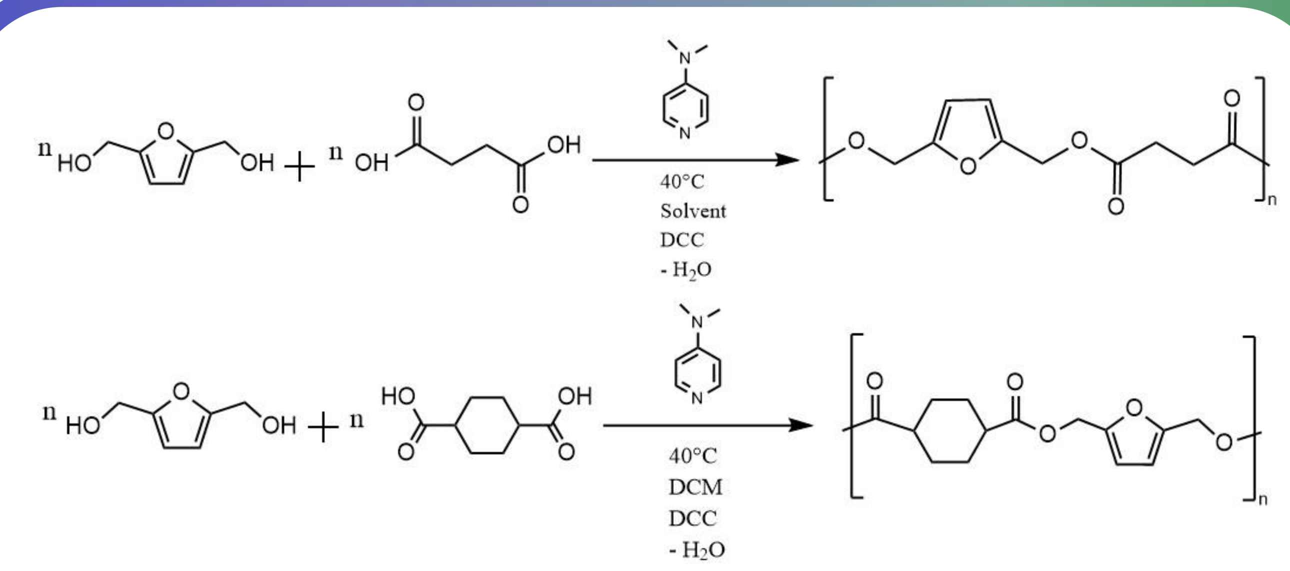
ABSTRACT

The concept of biorefinery focuses on generating chemical building blocks from biomass instead of fossil oil. Generally, the complex composition of biomass makes it possible to obtain a wide variety of molecules, which can then be further processed. Among these chemicals, **5-hydroxymethylfurfural** (HMF) stands out due to its significant potential. One of the most promising HMF derivatives, **2,5-bishydroxymethylfuran** (BHMF), has numerous possible applications, including as a biodiesel additive, non-ionic surfactant, monomer, or substrate in the flavour industry.[1] The **homogeneous catalytic** reduction of HMF to BHMF was investigated using **Shvo's catalyst**, achieving over **99% yield and selectivity** for BHMF under mild conditions and hydrogen atmosphere.[2] Now, a robust procedure for scaling up this process was successfully developed, obtaining good catalyst recyclability and using green solvents such as anisole. The resulting BHMF was then used as a bio-derived diol to create innovative **polyesters**. First polymerization experiments, following literature mechanisms[3], yielded good results. The reaction conditions were optimized, by selecting the best solvent and the most efficient reacting time. The use of different reagents, such as aliphatic dicarboxylic acids, is currently under study, with promising results.

OUR WORK



		HMF (mol/L)	Catalyst (mol%)	Time (h)	Solvent (160 mL)	PH_2 (bar)	Cooling time (h)
Series	**A**	0.150	0.1	1	Toluene	20	1.30
	B	0.225				30	
	C	0.150					
	D	0.300					
	E	0.150			Anisole		
	F	0.300					
	G	0.300	0.2				



RESULTS & DISCUSSION

YIELD

Cycle	A series	B series	C series	D series	E series	F series	G series
1	88%	96%	96%	96%	95%	95%	95%
2	90%	95%	96%	96%	92%	94%	96%
3	82%	89%	93%	96%	90%	93%	93%
4	71%	70%	91%	88%	81%	89%	97%
5	57%	65%	89%	81%	73%	86%	90%
6	51%	60%	84%	78%	70%	80%	78%
7	19%	42%	68%	47%	44%	75%	70%
8	-	-	60%	-	-	72%	57%
9	-	-	23%	-	-	60%	-

Each series reach the 7[th] **cycle** of the catalyst.

The **F** series, with **anisole** instead of toluene, is the most promising one as it allows **9 cycles** with high yields.

PURITY

Cycle	A series	B series	C series	D series	E series	F series	G series
1	100%	100%	100%	100%	100%	100%	100%
2	100%	99%	100%	99%	100%	100%	100%
3	100%	99%	100%	99%	100%	100%	100%
4	100%	94%	100%	94%	100%	100%	100%
5	80%	83%	99%	88%	100%	98%	100%
6	80%	76%	99%	85%	100%	97%	99%
7	50%	65%	82%	64%	97%	94%	95%
8	-	-	73%	-	-	91%	91%
9	-	-	70%	-	-	88%	-

The ones in **anisole** have a higher percentage of purity, even after the 8[th] cycle.

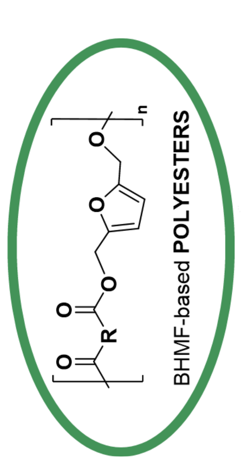
REACTION EFFICIENCY

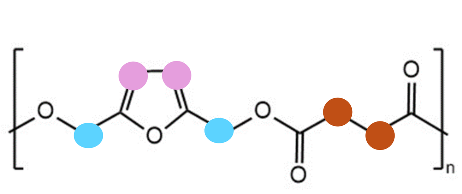
Series	Converted HMF	Selectivity	TON	D_r (h^{-1}) *
A	65%	100%	4449	2170
B	74%	100%	5060	2450
C	88%	100%	5526	2937
D	83%	100%	5684	2477
E	82%	100%	5521	2579
F	87%	100%	5931	2621
G	87%	100%	3064	1605

*** D_r = Productivity = (gBHMF/gRu/ reaction time)**

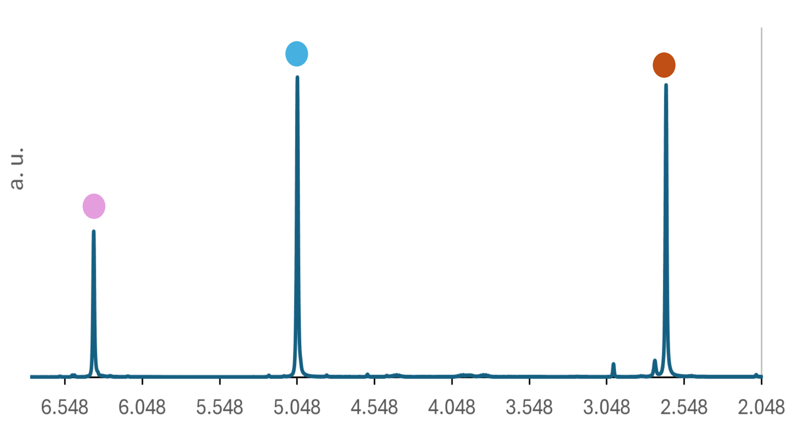
Catalyst deactivation due to **H_2O** increase (impurity) in consecutive cycles.

BHMF + Succinic acid

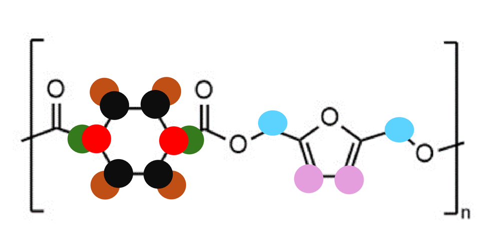




Mn 10000/ Mw 16000 in 1h

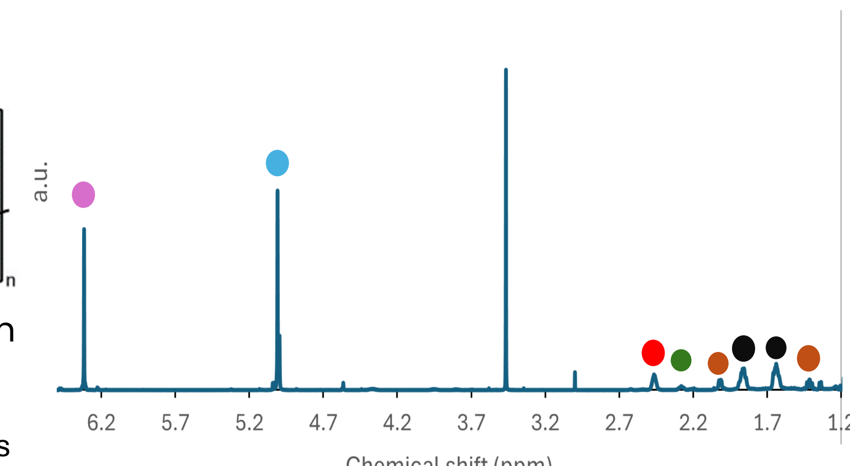


BHMF + 1,4-Cyclohexanedicarboxylic acid



Mn= 8400, Mw= 12000 in 1h

= CH cis = CH_2 cis
= CH trans = CH_2 trans



The structures of the new polymers are confirmed by **H-NMR analysis.** Characterizations are in progress.

It is noteworthy that the new polymers are potentially **fully biobased**.

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