



## The chemical stability and biodegradability of furanic platform chemicals and their derivatives

Dr. Bogdan Ya. Karlinskii

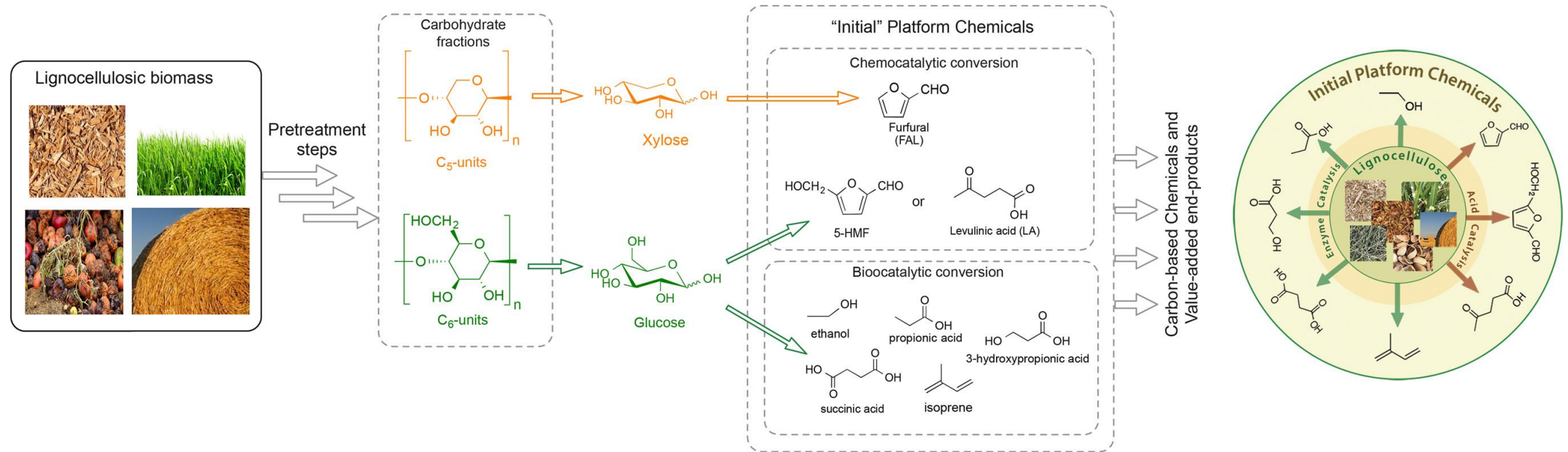
Tula State University, Russia

N. D. Zelinsky Institute of Organic  
Chemistry, Russian Academy of Sciences,  
Russia





# Platform chemicals – the foundation of the sustainable chemical industry



**Platform chemicals** are substances with high synthetic or fuel potential that can be produced from plant biomass during chemical or biotechnological conversion.

L. T. Mika, E. Cséfalvay, Á. Németh, *Chem. Rev.* **2018**, *118*, 505–613.

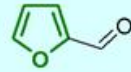
# Furanic platform chemicals



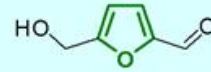
Benzene



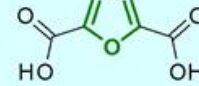
Furan



Furfural



5-(Hydroxymethyl)furfural



2,5-Furandicarboxylic acid



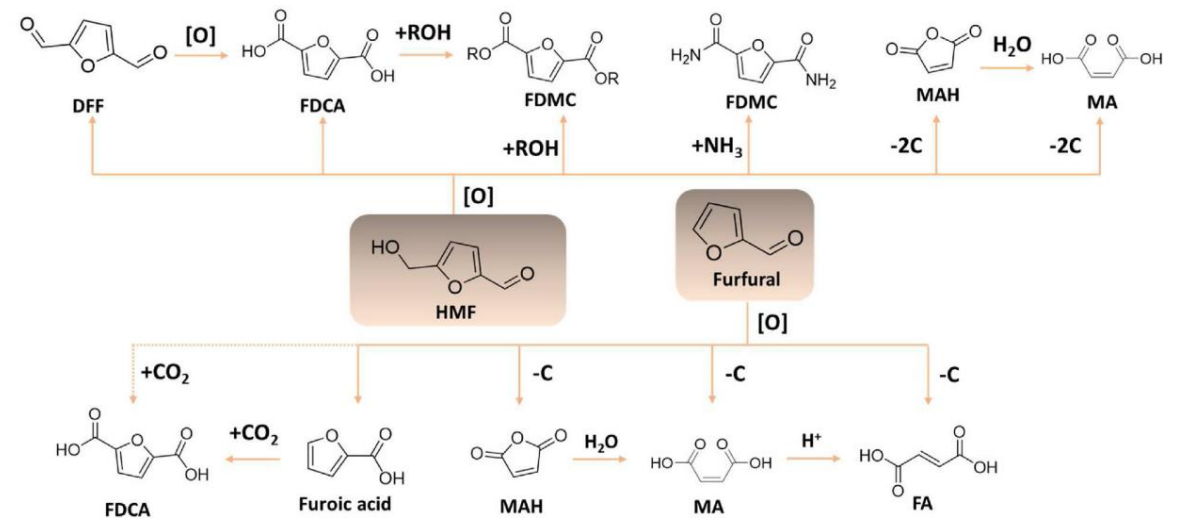
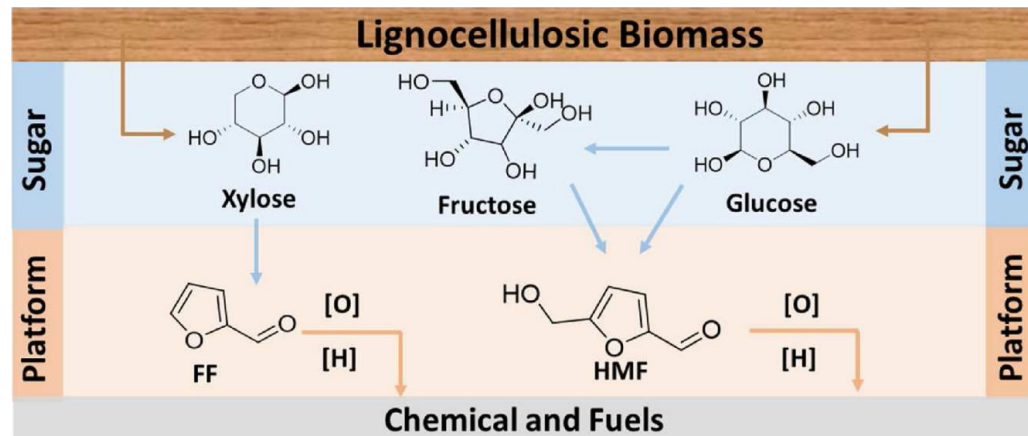
Carbonyl group  
in aldehydes



Hydroxyl group  
in alcohols

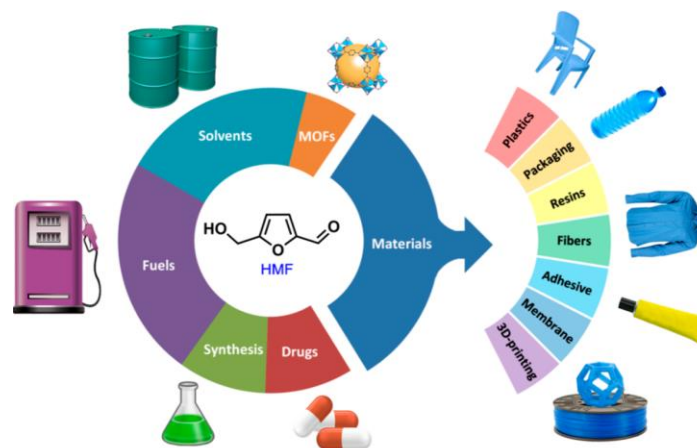
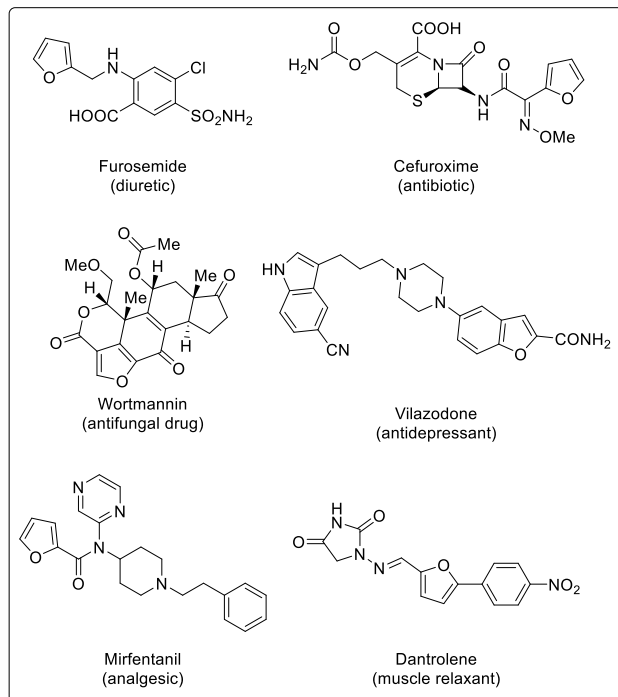


Carboxyl group  
in acids

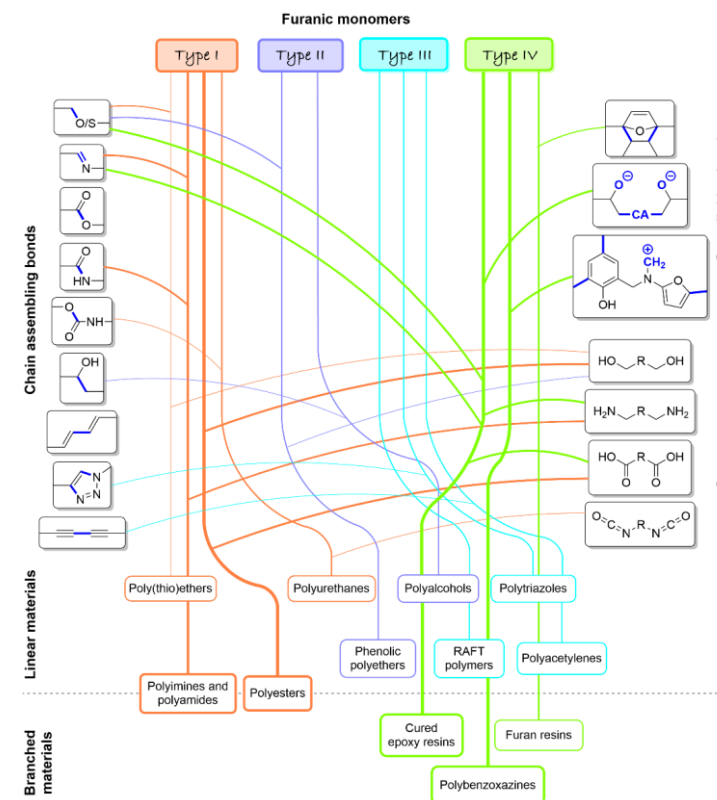


W. Deng, Y. Feng, J. Fu, H. Guo, Y. Guo, B. Han, Z. Jiang, L. Kong, C. Li, H. Liu, P. T. T. Nguyen, P. Ren, F. Wang, S. Wang, Y. Wang, Y. Wang, S. S. Wong, K. Yan, N. Yan, X. Yang, Y. Zhang, Z. Zhang, X. Zeng, H. Zhou, *Green Energy Environ.* **2023**, *8*, 10–114.

# Areas of application for furan platforms chemicals



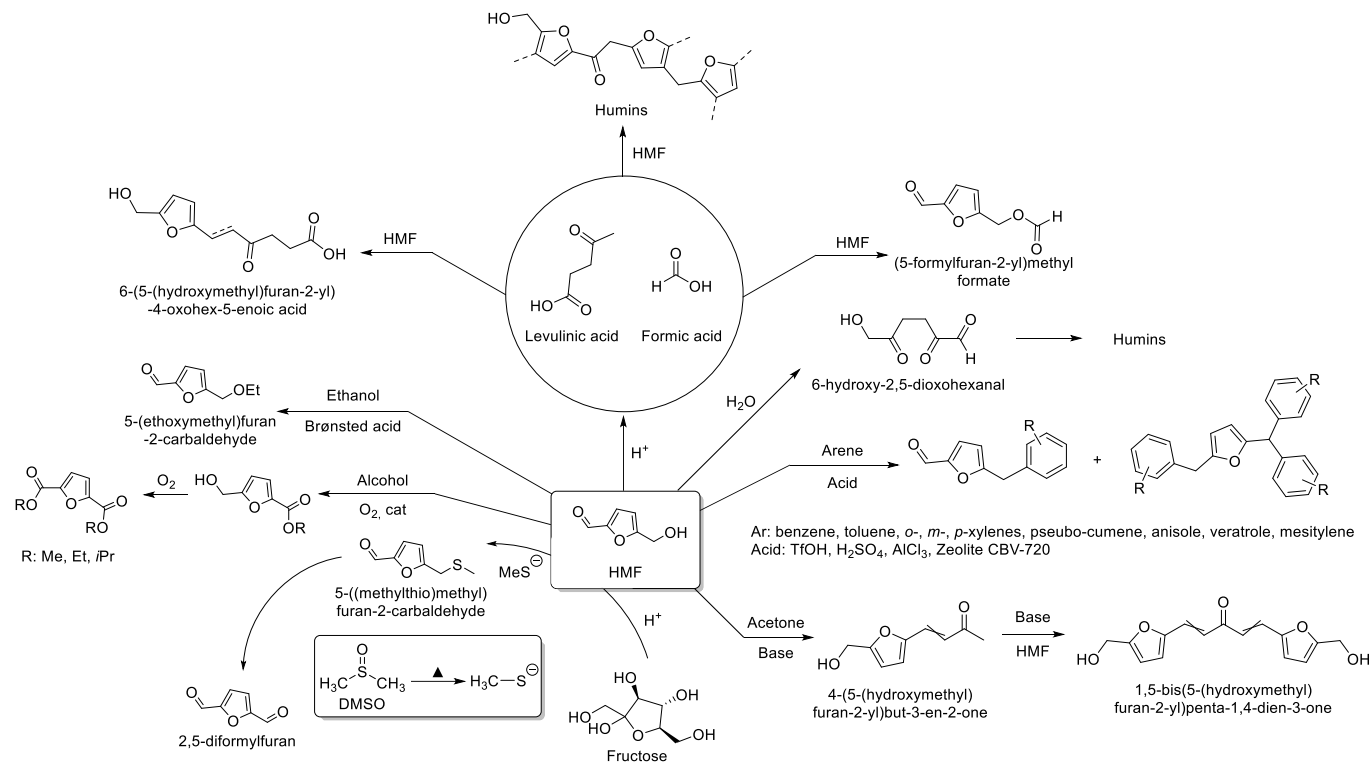
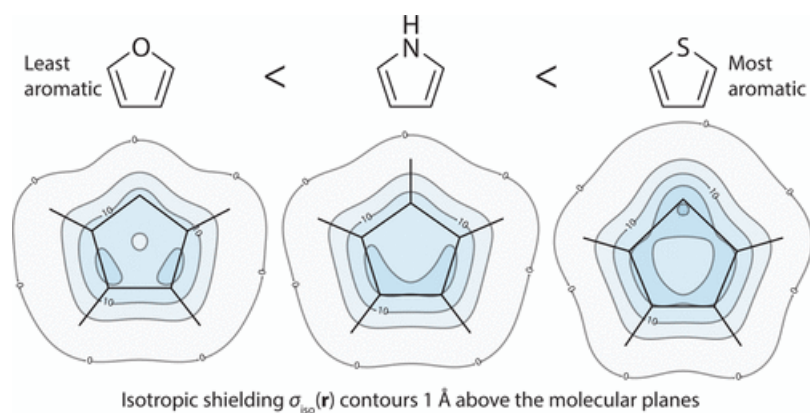
**HMF – «Sleeping Giant»  
of Sustainable Chemistry**



1. F. A. Kucherov, L. V. Romashov, K. I. Galkin, V. P. Ananikov, *ACS Sustainable Chem. Eng.* **2018**, *6*, 8064–8092.
2. B. Y. Karlinskij, V. P. Ananikov, *Chem. Soc. Rev.* **2023**, *52*, 836–862.



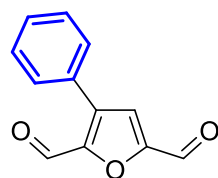
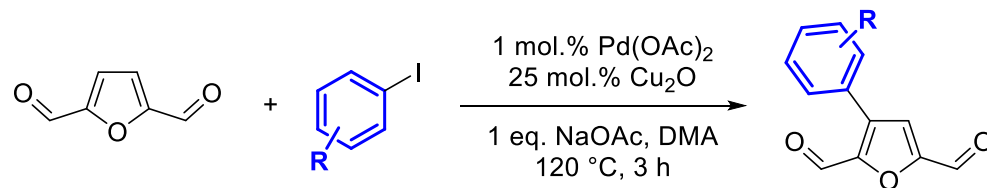
# Low aromaticity and high reactivity are the main challenges when working with furan derivatives



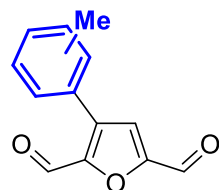
1. K. E. Horner, P. B. Karadakov, *J. Org. Chem.* **2013**, *78*, 16, 8037–8043
2. A. N. Golysheva, D. A. Kolykhalov, B. Y. Karlinskii, unpublished results



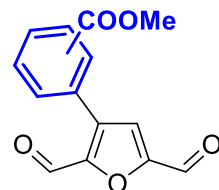
# Long road to reactions optimization



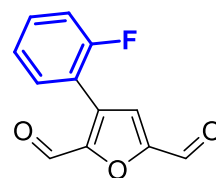
**4**, 74 (61) %



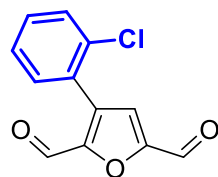
**6**, *o*-Me, 73 (63) %  
**7**, *m*-Me, 66 (59) %  
**8**, *p*-Me, 70 (63) %



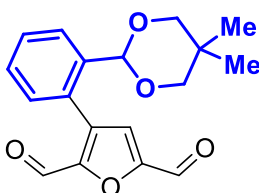
**9**, *o*-COOMe, 71 (58) %  
**10**, *m*-COOMe, 60 (51) %  
**11**, *p*-COOMe, 43 (36) %



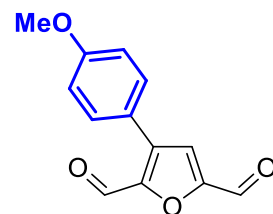
**12**, 59 (52) %



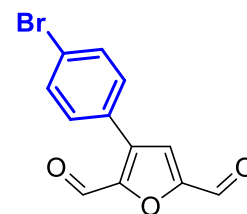
**13**, 66 (62) %



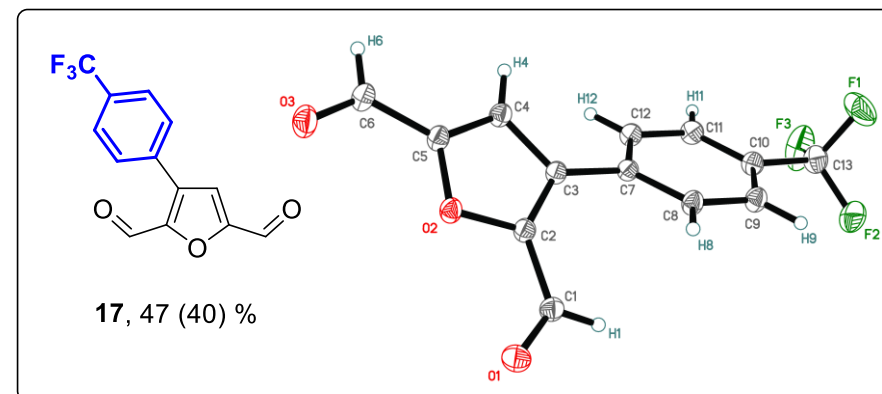
**14**, 72 (64) %



**15**, 71 (59) %



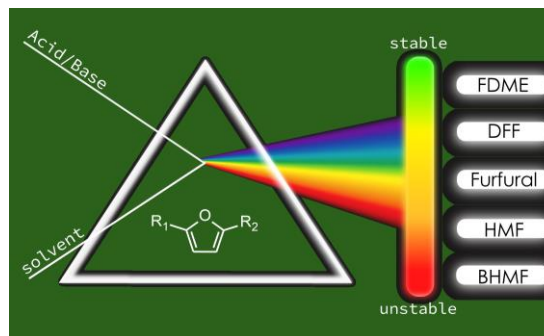
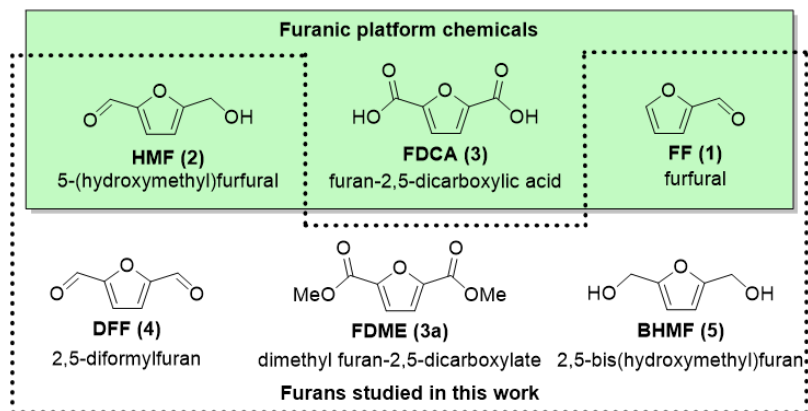
**16**, 55 (47) %



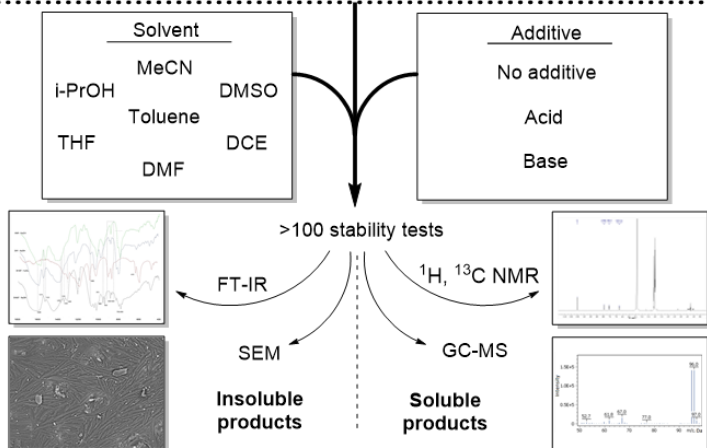
[B. Y. Karlinskij, A. Y. Kostyukovich, F. A. Kucherov, K. I. Galkin, K. S. Kozlov, V. P. Ananikov, \*ACS Catal.\* \*\*2020\*\*, \*10\*, 11466-11480](#)

[B. Y. Karlinskij, V. P. Ananikov, \*ChemSusChem\* \*\*2021\*\*, \*14\*, 558-568](#)

# Systematic stability test of furanic platform chemicals and their derivatives



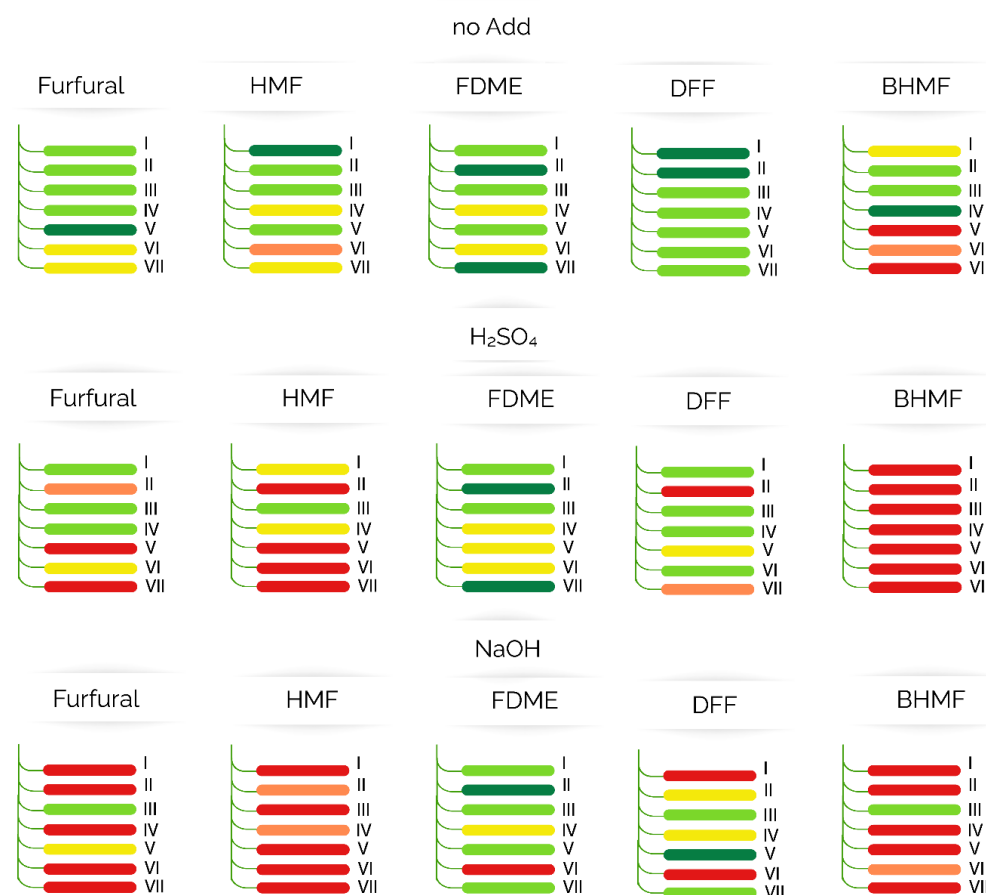
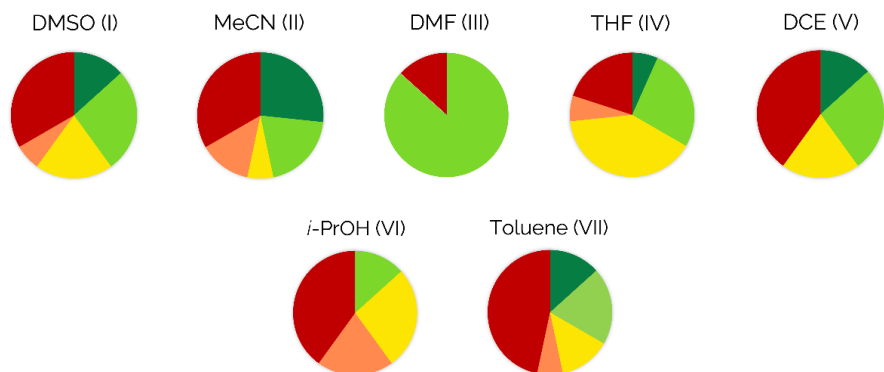
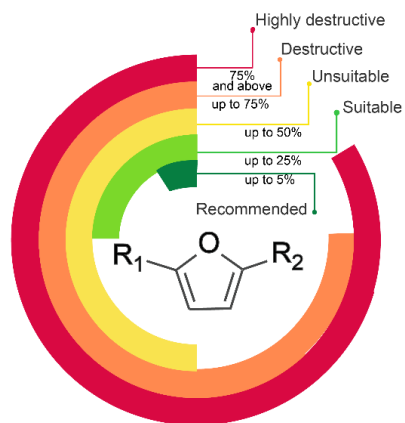
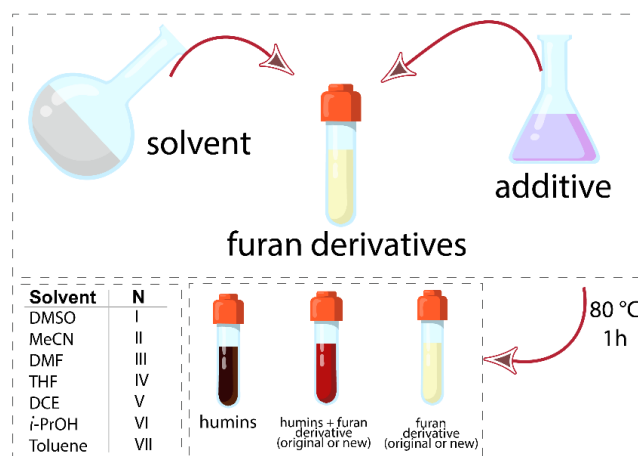
Solvent	Furfural		HMF		FDME		DFF		BHMF	
	NoAdd	H <sub>2</sub> SO <sub>4</sub> / NaOH	NoAdd	H <sub>2</sub> SO <sub>4</sub> / NaOH	NoAdd	H <sub>2</sub> SO <sub>4</sub> / NaOH	NoAdd	H <sub>2</sub> SO <sub>4</sub> / NaOH	NoAdd	H <sub>2</sub> SO <sub>4</sub> / NaOH
MeCN				34 37	88 89			58 71		
i-PrOH		23 25	36 37	45 46	53 54	63 64				
Toluene	24 25	37 38	48 49	90 91	92 93	61 62	75 76			
THF				38 40	52 53	63 64	74 75			
DMSO		30 32		42 43	53 54	65 66	67 68	79 80		
DMF				43 45	57 58	68 69	70 71			
DCE	45 46	47 48		45 46	32 34	35 36			84 85	



**FT-IR** – Fourier-transform infrared spectroscopy  
**SEM** – scanning electron microscopy  
**NMR** – nuclear magnetic resonance  
**GC-MS** – gas chromatography-mass spectrometry



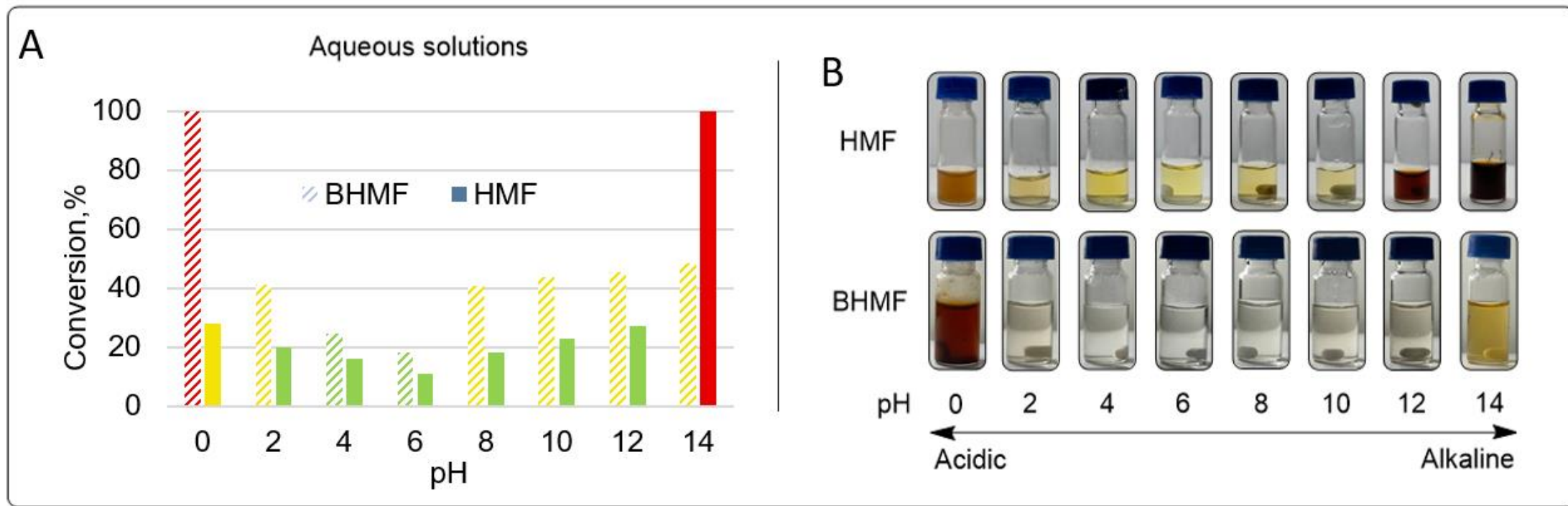
# Stability profiles of furans depending on the solvent used



D. A. Kolykhalov, A. N. Golyшева, K. S. Erokhin, [B. Y. Karlinskii](#), V. P. Ananikov, *ChemSusChem* **2024**, *17*, e202401849



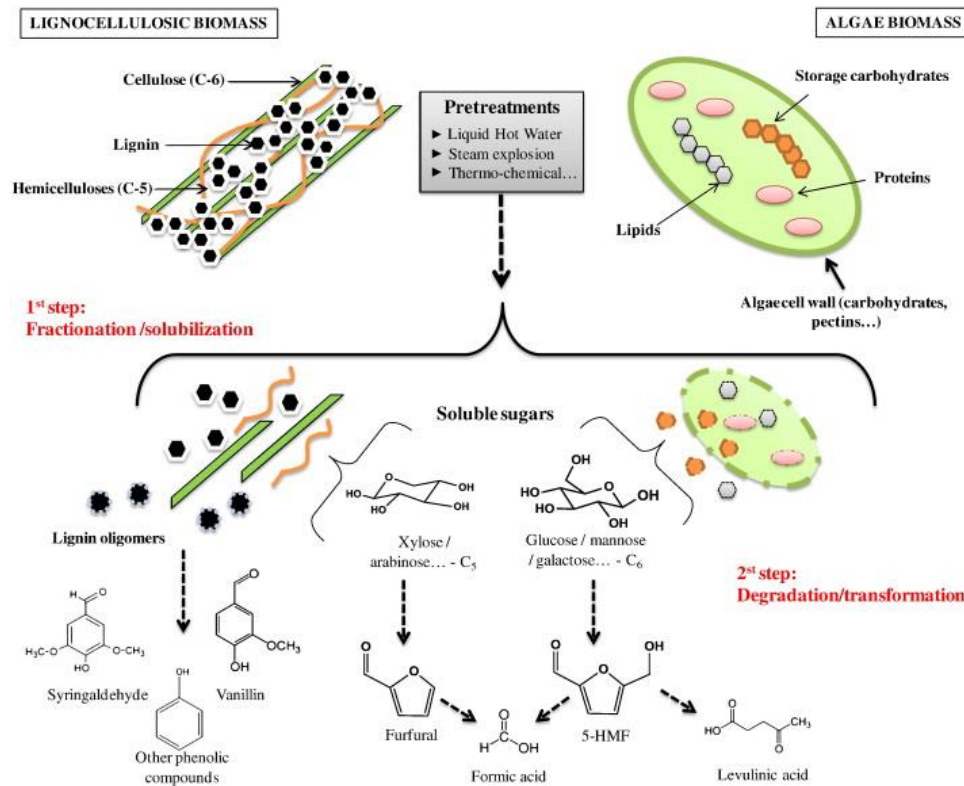
# Stability of HMF and BHMF in water solutions at different pH



D. A. Kolykhalov, A. N. Golysheva, K. S. Erokhin, [B. Y. Karlinskii](#), V. P. Ananikov, *ChemSusChem* **2024**, *17*, e202401849



# Furan substrates – friends or foes?

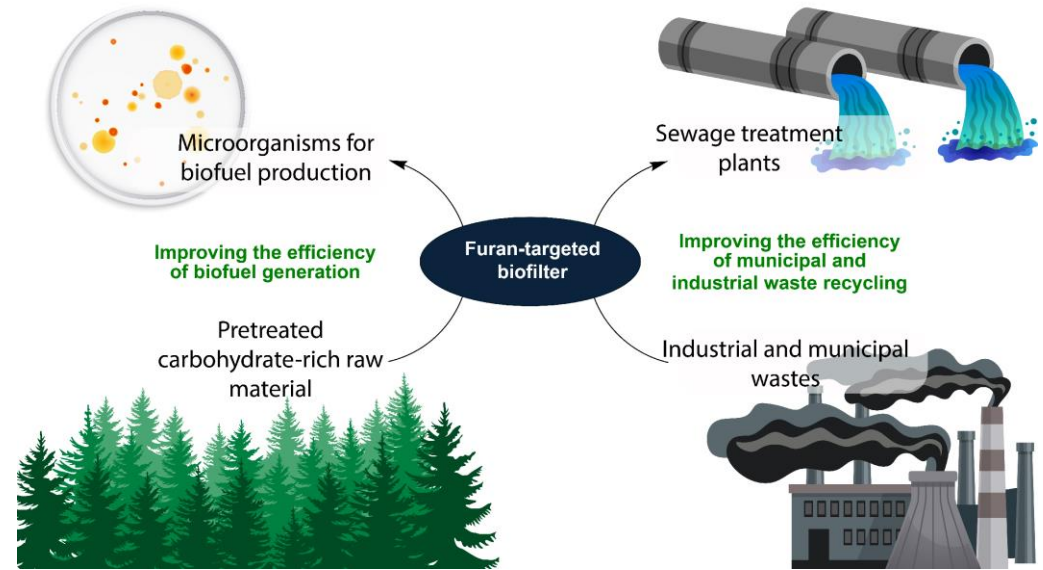
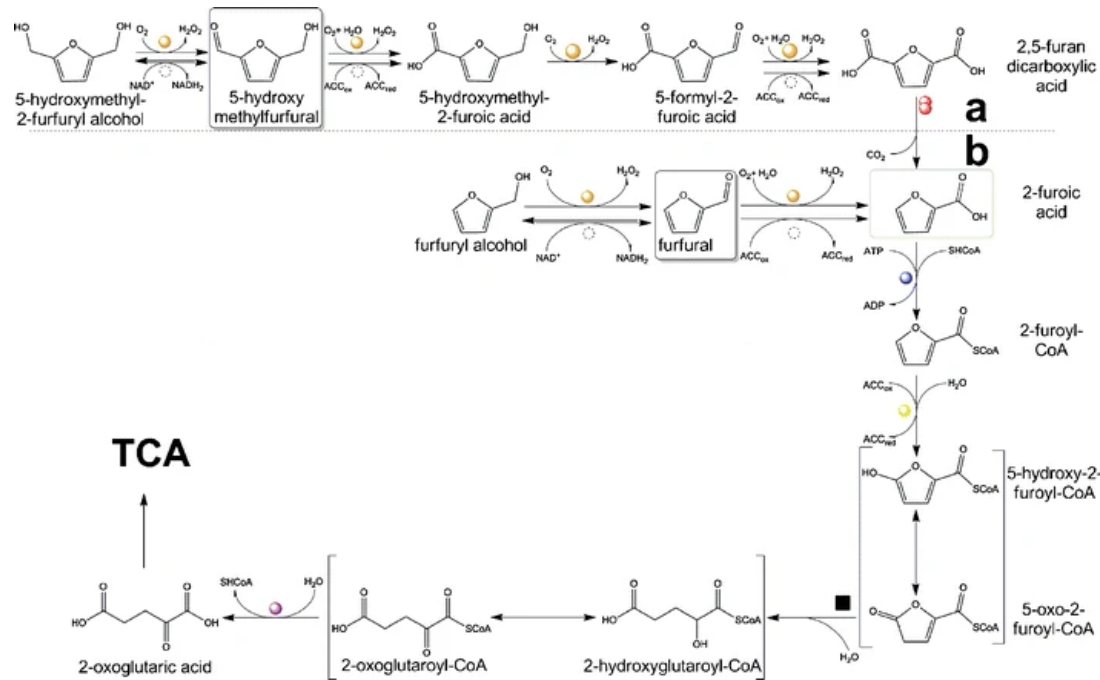


**Table 2** Experimental studies on inhibition caused by furaldehydes in various processes

Fermentation process	Microorganism	Inhibitor	Inhibitor conc. (g/L)	Productivity reduction (%)	Growth rate reduction (%)
Ethanol production	<i>S. cerevisiae</i>	Furfural	0.5–4.0	21–97	0–80
	<i>S. cerevisiae</i>	Furfural	1.0–2.0	0 <sup>a</sup> –40	7 <sup>a</sup> –13 <sup>a</sup>
			1.0–2.0	4 <sup>a</sup> –12 <sup>a</sup>	6–19
	<i>S. cerevisiae</i>	Furfural	0.9–5.1	18–87	28–100
	<i>S. cerevisiae</i>	Furfural	1–5	4 <sup>b</sup> –100 <sup>b</sup>	51 <sup>c</sup> –91 <sup>c</sup>
			1–5	1 <sup>b</sup> –44 <sup>b</sup>	4 <sup>c</sup> –39 <sup>c</sup>
	<i>S. cerevisiae</i>	Furfural	4	56	89
	<i>S. cerevisiae</i>	Furfural	1.0–2.0	1 <sup>d</sup> –99 <sup>d</sup>	–
	<i>S. cerevisiae</i>	Furfural	0.5–2.0	43–89	47–90
	<i>S. carlsbergensis</i>	Furfural	1–10	35 <sup>a</sup> –100 <sup>a</sup>	–
<i>S. cerevisiae</i>	HMF	2–4	19–41	40–71	

J. R. M. Almeida, M. Bertilsson, M. F. Gorwa-Grauslund, S. Gorsich, G. Lidén, *Appl. Microbiol. Biotechnol.* **2009**, *82*, 625–638  
 F. Monlau, C. Sambusiti, A. Barakat, M. Quéméneur, E. Trably, J.-P. Steyer, H. Carrère, *Biotechnol. Adv.* **2014**, *32*, 934–951

# Furans bioprocessing for improving the efficiency of biotechnology treatment

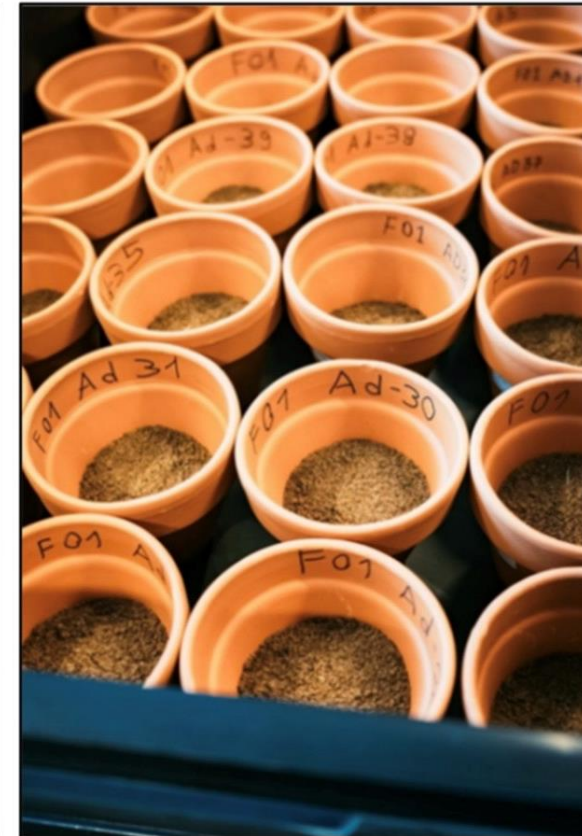
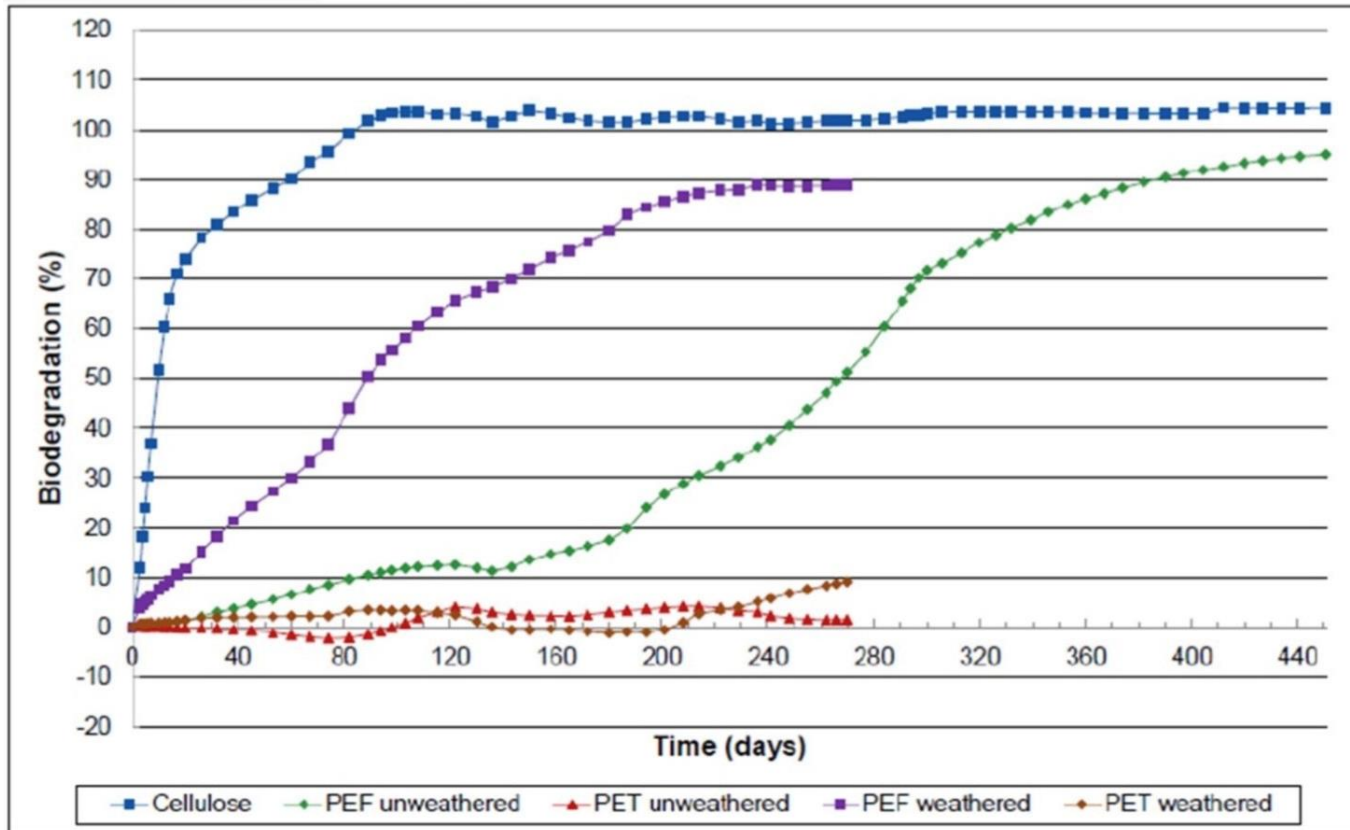


Grant of PhosAgro/UNESCO/IUPAC Partnership in Green Chemistry for Life № 8050 «*Furanic platform chemicals biodegradation study for bacterial processing of industrial waste*»

Grantee – Dr. B. Ya. Karlinskii



# Comparison of PET and PEF biodegradability



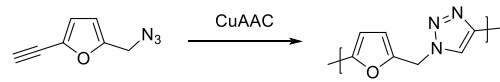
E. De Jong, H.A. Visser, A.S. Dias, C. Harvey, G.-J. M. Gruter, *Polymers* **2022**, 14, 943





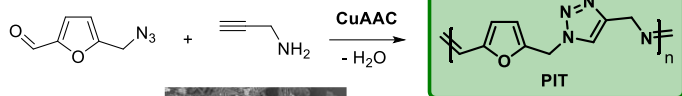
# Biodegradable click-synthesized materials

## 1. Known

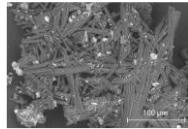


- ✗ Low molecular weight
- ✗ Poor thermal stability
- ✗ Low-stable monomer

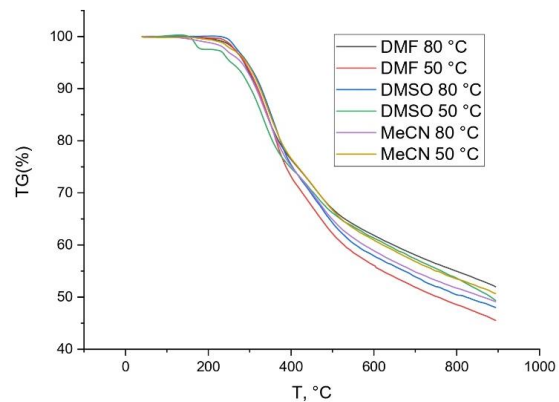
## 2. This work



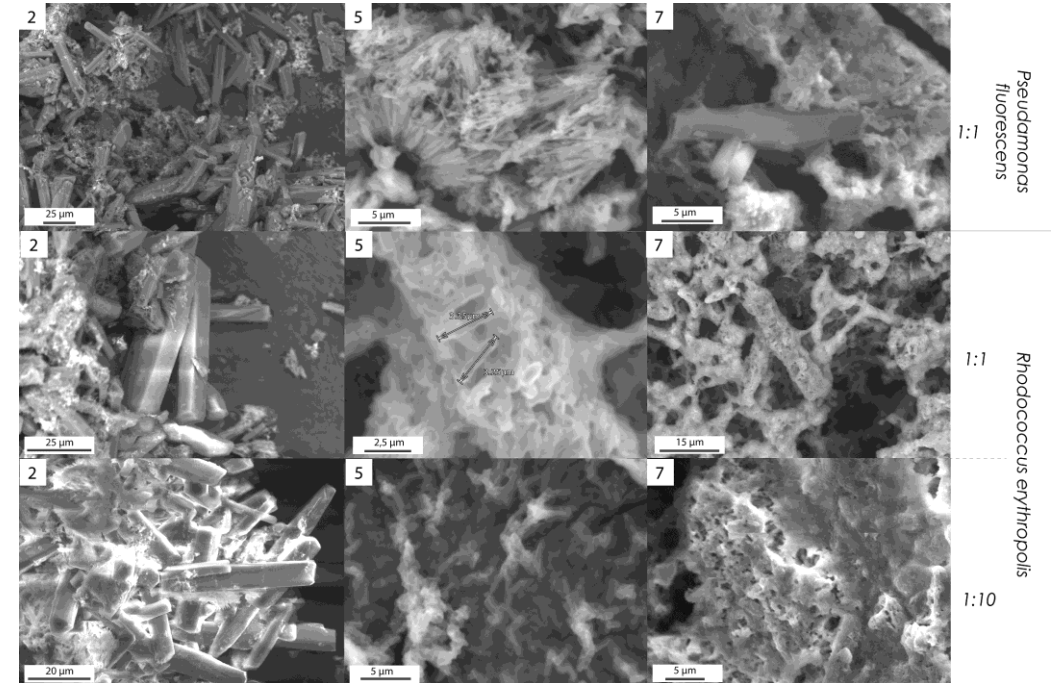
SEM image of the prepared material morphology



- ✓ Novel renewable materials
- ✓ Thermal stability up to 290 °C
- ✓ Carbon yield up to 53%
- ✓ Biodegradability



Nº	Conditions	T <sub>d5</sub>	T <sub>d10</sub>	CY, %	LOI
1	DMF, 80 °C	286.7	317.7	46.5	38.9
2	DMF, 50 °C	290.3	321.2	52.9	36.3
3	DMSO, 80 °C	293.7	328.0	50.7	37.2
4	DMSO, 50 °C	256.0	304.0	48.4	38.1
5	MeCN, 80 °C	280.0	317.7	49.6	37.7
6	MeCN, 50 °C	293.7	324.6	47.8	38.3

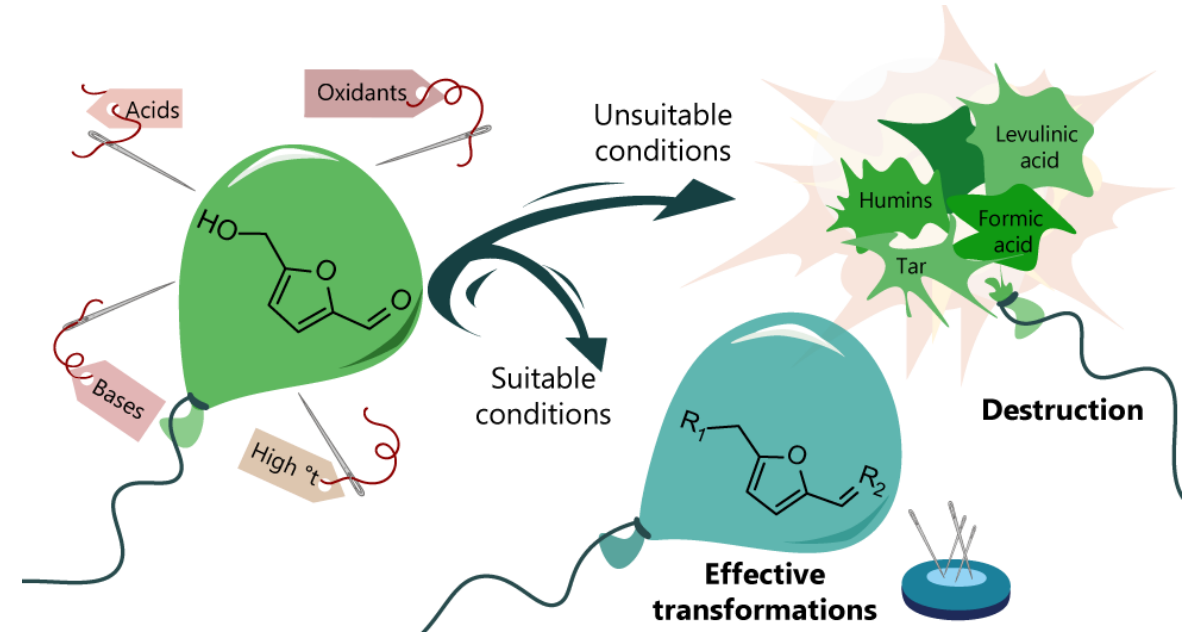
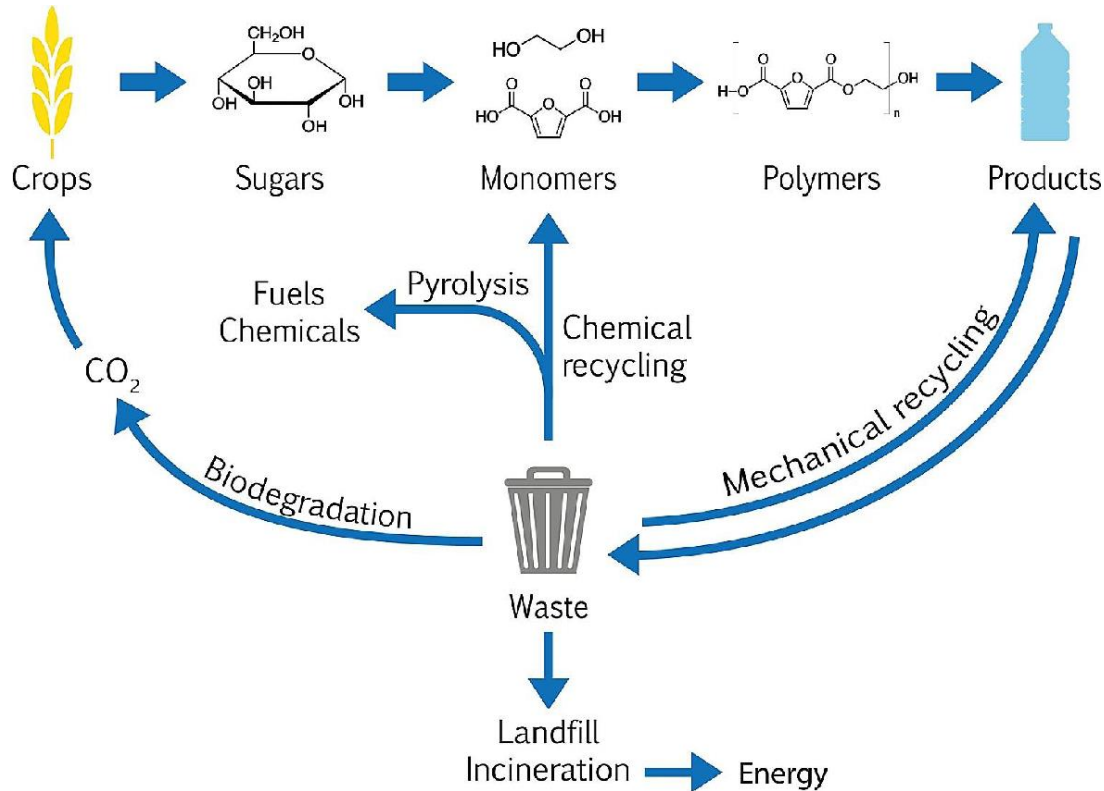


SEM images of *R. erythropolis* and *P. fluorescens* biofilm formation and growth on PIT samples after 2, 5, and 7 days of treatment. The weight ratios of polymer and microorganisms are shown on the right

D. A. Kolykhalov, D. S. Gurov, A. N. Golyshva, V. G. Krasheninnikov, B. Y. Karlinskii, unpublished results



# Furan derivatives – an unstable pillars of a sustainable future



L. Silverwood, M. Mottoul, M.-J. Dumont, *J. Polym. Environ.* **2024**, *32*, 4130–4142  
 A. N. Golysheva, D. A. Kolykhalov, B. Y. Karlinskij, unpublished work

# Thank you for your attention!

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[karbo@tsu.tula.ru](mailto:karbo@tsu.tula.ru)

