Energy-efficient and eco-friendly continuous production of 5-CMF in a UV-Ultrasound irradiated catalytic packed bed reactor: heterogeneous kinetics, reactor simulation and LCA analysis

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S1. Conversion analysis:

Soluble starch (SS) conversion, glucose yield, 5-HMF yield and 5-CMF yield were calculated according to the below equations

$$SS\ conversion = [\frac{\text{Initial SS } (g) - \text{Final SS } (g)}{\text{Initial SS } (g)}] \times 100 \quad (1)$$

$$Glucose\ yield\ (Y_G) = [\frac{\text{Glucose produced } (g)}{\text{Initial SS } (g) \times 1.111}] \times 100 \quad (2)$$

$$5-HMF\ yield\ (Y_{HMF}) = [\frac{\text{5 - HMF produced } (g)}{\text{Initial SS } (g) \times 0.7778}] \times 100 \quad (3)$$

$$5-CMF\ yield\ (Y_{CMF}) = [\frac{\text{5 - CMF produced } (g)}{\text{Initial SS } (g) \times 0.8915}] \times 100 \quad (4)$$

The denominating factor 1.111, 0.7778 and 0.8915 accounts for the mass accumulation or mass reduction during conversion of repeating units of starch to glucose, 5-HMF and 5-CMF respectively [1].

Table S1. L-9 Taguchi orthogonal design for 5-CMF synthesis

$\emptyset_T$	$\emptyset_t$	$\emptyset_{S101/TiO_2}$	$\emptyset_{ChCl/SS}$	Y_{CMF}	S.D.
60	30	0.5	1	18.10	± 0.50
60	60	1.5	3	30.23	± 0.80
60	90	2.5	5	39.00	± 1.00
70	30	1.5	5	45.4	± 0.30
70	60	2.5	1	33.10	± 0.50
70	90	0.5	3	35.00	± 0.50
80	30	2.5	3	37.82	± 0.25
80	60	0.5	5	58.27	± 0.50
80	90	1.5	1	41.10	± 0.20

S2. Analyses of the external mass transfer resistance between reactants and solid catalysts

Mear's criterion (Ω) (Equation-5) was employed to analyse the external diffusion-controlled regimes [2]. According to Mear's criterion, Ω < 0.15, implied negligible external mass transfer diffusion resistance; whereas, Ω > 0.15, inferred that the reaction was external mass transfer resistance limited.

$$\Omega = \frac{nr\ \rho_C R_C}{K_m C} < 0.15 \ldots\ldots\ldots\ldots(5)$$

Where n: reaction's order; R_C (m): radius of the catalyst (S-101 or TiO_2) [In the calculation of Ω for the SS hydrolysis, glucose dehydration, and 5-HMF chlorination steps, only the catalyst radius relevant to each specific reaction step was taken into consideration]; r (Kmol /kg cat. s): maximum observed reaction rate for SS hydrolysis, glucose dehydration, and 5-HMF chlorination steps. K_m (m/s): mass transfer coefficient; ρ_C (kg / m^3): catalyst bulk density; C (Kmol / m^3): bulk concentration of limiting reactant (SS, glucose, 5-HMF). K_m was calculated using the following Equation-6 [3].

$$\frac{2R_C K_m}{D} = 2.0 + 0.6\left(\frac{2R_C V}{\vartheta}\right)^{\frac{1}{2}}\left(\frac{\vartheta}{D}\right)^{\frac{1}{3}} \ldots\ldots\ldots\ldots(6)$$

Where D (m^2/s): diffusion coefficient of reactants viz., SS, glucose and 5-HMF through reaction medium; ϑ (m^2/s): kinematic viscosity of reaction mixture; V (m/s): velocity of reactants approaching catalyst. The velocity (V) of reactants under ultrasound has been calculated according to Frenkel et al. [4].

$$V = \frac{(0.0992 \times I_{US})}{100} ....(7)$$

Where, I_{US} is the intensity of ultrasound in W/cm^2.

The D of reactants was evaluated using Wilke-Chang equation as per Equation-8.

$$D = 1.173 \times 10^{-16}(\theta M_W)^{\frac{1}{2}}\frac{T}{\mu_{mix}(V_m)^{0.6}} ....(8)$$

Where θ: the association parameter (2.26 for water) [5]; M_W (kg/mol): molecular weight of water; μ_{mix} (kg/m s): bulk viscosity of reaction mixture; V_m (m^3/kg mol): molar volume of reactants at the boiling point. The bulk viscosity and kinematic viscosity of the individual components as well as molar volume of the reactants were calculated from ASPEN PLUS software. The μ_{mix} were calculated according to equation-9.

$$\mu_{mix} = \sum_{1}^{n} x_i \mu_i ....(9)$$

Here n is the total number of components, x_i represents the mole fraction of i-th component and μ_i represent the bilk viscosity of the i-th component.

S3. Synthesis of TiO_2 coated glass beads

To prepare the TiO_2 coated glass beads, the surface of the glass beads was initially roughened through a chemical etching process by immersing the glass beads in hydrofluoric acid for a duration of 24 hours. Subsequently, the nano TiO_2 powder and HF-treated glass beads were mixed in an acetone medium at a temperature of 70°C. The mixing process was conducted under magnetic stirring conditions at 300 rpm for a period of 3 hours. Following this, the mixture was subjected to oven drying and finally calcined at a temperature of 300°C for a duration of 3 hours to produce TiO_2 coated glass beads (Fig. S1) with average beads size of 4 mm and average coating thickness of 0.2 mm. According to the BET analysis, the TiO_2 coating applied to the glass beads was found to be non-porous, exhibiting an extremely low amount of average pore volume (0.021 cm^3/g) and an average pore diameter (1.27 nm) that was negligible. The TiO_2 loading weight was determined by measuring the difference between the weight of the glass beads before and after the TiO_2 coating process.

Fig. S1. TiO_2 coated glass beads

S4. RTD analysis for UVUS-RPBR

In pulse tracer experiment, water was used as eluent with the flow rate of 126 ml/h and blue Dextran was used as tracer material which was injected in one shot for the evaluation of the residence time distribution (RTD) parameters of the RPBR with bed porosity of 0.56. The tracer concentrations at outlet stream were measured using a UV-VIS detector at 300 nm and exit-age distribution function (E(t)) with respect to time was evaluated. The Peclet number (*Pe*) was calculated considering 'closed-closed' Danckwerts boundary conditions as per Equation-10.

$$\frac{\sigma^2}{{\tau_{mean}}^2} = \frac{2}{Pe} - \frac{2}{Pe^2}(1 - e^{-Pe}) \qquad (10)$$

Where $Pe = \frac{UL}{D}$

Here, L is the reactor length, U is the superficial velocity of water, D is the dispersion number.

Table S2. LCI data for production of 1 kg of TiO_2 coated glass beads

Category	Flow	Value	Unit	Source	Comments
Energy Input	Electricity consumed	3.3	kWh	Ecoinvent-3.5	
Material Input	Hydrofluoric acid	0.5	Kg	Ecoinvent-3.5	
	TiO_2	0.1	Kg	Ecoinvent-3.5	
	Glass beads	1.0	Kg	Ecoinvent-3.5	
Transports	Hydrofluoric acid	0.0031	Kg.km	Ecoinvent-3.5	Transport by lorry, capacity: 16 metric ton, EURO VI (assuming all materials came from 100 km distance)
	TiO_2	0.000625	Kg.km	Ecoinvent-3.5	
	Glass beads	0.005625	Kg.km	Ecoinvent-3.5	
	Total	**0.00935**	**Kg.km**	Ecoinvent-3.5	
Emissions to air	Waste heat	11.8	MJ	Ecoinvent-3.5	Assuming electrical energy used was dissipated as heat to air (1 kWh =3.6 MJ)
Waste of materials	Sludge	0.6	kg	Ecoinvent-3.5	Generated during hydrofluoric acid treatment
Output	TiO_2 coated glass beads	1	Kg	Created	

Table S3. LCI data for production of 1 kg of CMF production in UVUS-RPBR

Category	Flow	Value	Unit	Source	Comments
Energy Input	Electricity consumed	0.365	kWh	Ecoinvent-3.5	
Material Input	Starch	1.91	Kg	Ecoinvent-3.5	As remaining choline chloride, water recycled back.
	Choline chloride	0.965	Kg	Ecoinvent-3.5	
	Water	0.0346	Kg	Ecoinvent-3.5	All cyclohexane was recycled, except for a 5 % volume loss during recycling.
	Cyclohexane	0	Kg	Ecoinvent-3.5	
	Smopex-101	0.0192	Kg	Created	
	TiO_2 coated glass beads	0.127	Kg	From Table 2S	Catalysts recycling up to 6 times.
	Ethanol	0.10	kg	Ecoinvent-3.5	For choline chloride separation.
Transports	Starch	0.012	Kg.km	Ecoinvent-3.5	Transport by lorry, capacity: 16 metric ton, EURO VI (assuming all materials came from 100 km distance)
	Choline chloride	0.006	Kg.km	Ecoinvent-3.5	
	Water	0.00022	Kg.km	Ecoinvent-3.5	
	Cyclohexane	0.012	Kg.km	Ecoinvent-3.5	
	Smopex-101	0.00012	Kg.km	Ecoinvent-3.5	
	TiO_2 coated glass beads	0.0008	Kg.km	Ecoinvent-3.5	
	Ethanol	0.000625	Kg.km	Ecoinvent-3.5	
	Total	**0.0318**	**Kg.km**	Ecoinvent-3.5	
Emissions to air	Waste heat	1.314	MJ	Ecoinvent-3.5	Assuming electrical energy used was dissipated as heat to air (1 kWh =3.6 MJ)
	Water vapour	0.084	kg		
Output	5-CMF	1	Kg	Created	
	Glucose	0.345	Kg	Ecoinvent-3.5	
	5-HMF	0.202	Kg	Created	

Table S4. Purification of 1 kg of 5-CMF

Category	Flow	Value	Unit	Source	Comments
Energy Input	Electricity consumed	0.125	kWh	Ecoinvent-3.5	
Material Input	5-CMF	1	kg	From Table 3S	

Emissions to air	Waste heat Cyclohexane	0.45 0.95	MJ Kg	Ecoinvent-3.5	Assuming electrical energy used was dissipated as heat to air (1 kWh =3.6 MJ) (5 % of volume loss of total used cyclohexane)
Output	Purified 5-CMF	1	Kg	Created	

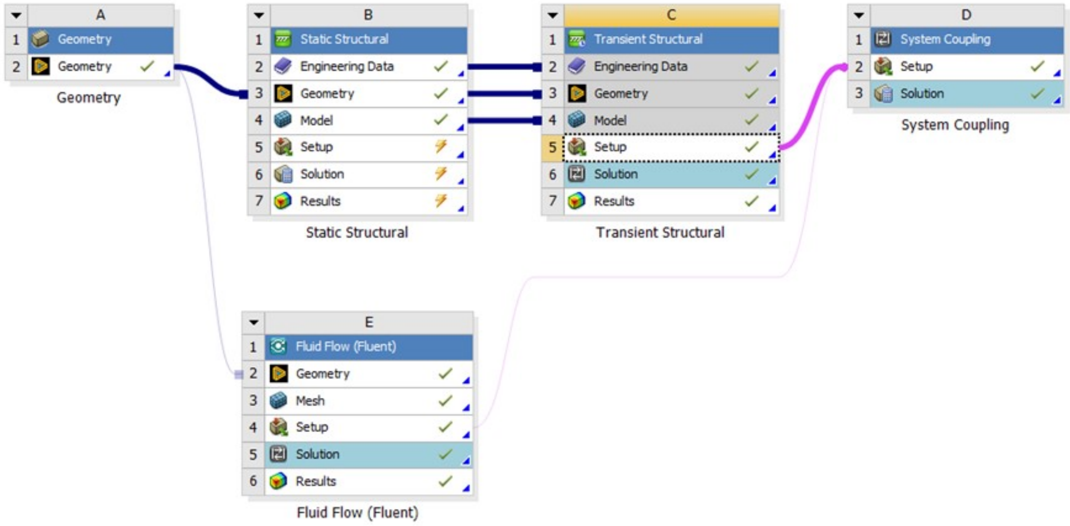

Fig. S2. ANSYS Transient Structural and ANSYS Fluent coupling for the simulation of UVUS-RPBR

	A	B	C	D	E
1	Property	Value	Unit		
2	Material Field Variables	Table			
3	Density	4500	k...		
4	Isotropic Secant Coefficient of Thermal Expansion				
6	~~Isotropic Elasticity~~			☑	
7	Derive from	Young's Modulus ...			
8	Young's Modulus	2E+11	Pa		
9	Poisson's Ratio	0.3			
10	Bulk Modulus	1.6667E+11	Pa		
11	Shear Modulus	7.6923E+10	Pa		
12	Orthotropic Elasticity				
13	Young's Modulus X direction	7.856E+10	Pa		
14	Young's Modulus Y direction	7.856E+10	Pa		
15	Young's Modulus Z direction	6.2498E+10	Pa		
16	Poisson's Ratio XY	0.28798			
17	Poisson's Ratio YZ	0.45204			
18	Poisson's Ratio XZ	0.45204			
19	Shear Modulus XY	3E+10	Pa		
20	Shear Modulus YZ	2.6E+10	Pa		
21	Shear Modulus XZ	2.6E+10	Pa		
22	Strain-Life Parameters				
30	S-N Curve	Tabular			
34	Tensile Yield Strength	2.5E+08	Pa		
35	Compressive Yield Strength	2.5E+08	Pa		
36	Tensile Ultimate Strength	4.6E+08	Pa		
37	Compressive Ultimate Strength	0	Pa		

Fig. S3. Piezoelectric material properties

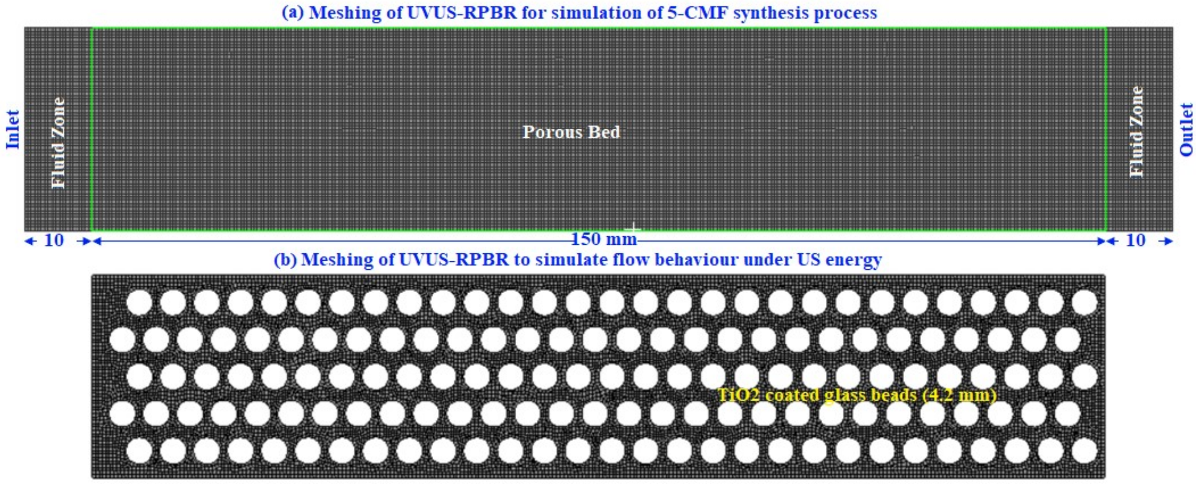

Fig. S4. Meshing of UVUS-RPBR for the simulation study

Table S5. Operational parameter for transient simulation

Parameters	Values
Temperature (K)	353
Pressure (Pa)	101325
Superficial aqueous liquid feed velocity (m/s)	4.1E-5
Reactor width (m)	0.05
Reactor height (m)	0.03
Reactor length (m)	0.15
Bed porosity	0.56
TiO_2 coated glass beads diameter (m)	0.0042
Mesh size (m)	0.0005
Step size	0.1
Time steps	36000

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