Electronic Supplementary Material (ESI) for RSC Sustainability.

Continuous drop-in-biofuel production from pretreated sugarcane bagasse in Microwave-Visible irradiated continuous stirred slurry reactor: Reaction kinetics & techno-enviro-economic sustainability analyses

Sourav Barman [a] and Rajat Chakraborty [a]*

[a]Chemical Engineering Department, Jadavpur University, Kolkata-700032, India
*Corresponding Author, Tel: +91 3324572689; fax: +91 3324146378
Email: rajat_chakraborty25@yahoo.com; rajat.chakraborty@jadavpuruniversity.in

S1. Pretreatment of sugarcane bagasse (SCB)

Prior to the pretreatment process, the collected SCB first thoroughly washed with deionized water and oven dried at 70° C. The dried SCB was then grinded into fine powder **(**size range: -240+300 mesh**)** using ball milling. In delignification step, 50 g of the dried SCB powder was treated with 100 ml of peracetic acid (99% glacial acetic acid: 30% H_2O_2 of 7:3 vol/vol) at 80 °C [1]. Afterwards, the resulting mixture was then filtered and the filter cake was washed with hot water for several times to obtain the pretreated-SCB (PSCB). On the other hand, the filtrate was neutralized with NaOH, and the precipitated lignin was separated. Finally, compositional analysis (cellulose, hemicellulose and lignin) and elemental analysis (CHNS analysis) of both SCB powder and PSCB were done, which are tabulated in the Table 1S.

Table S1. Compositional analysis of SCB and PSCB

CHNS analysis	SCB	PSCB	Compositional analysis*	SCB	PSCB
C	40.17	33.42	Cellulose	37.5	49.3
H	5.91	3.95	Hemicellulose	29.3	39.5
N	0.28	0.86	Lignin	23.50	4.3
S	0.008	0.012			

* Compositional analysis was done based on Anthrone method [2]

S2. EL purification and DES recycling

After completion of EL synthesis process from pretreated sugarcane bagasse, the reaction mix were separated according to the following steps as demonstrated in Fig S1. Initially, the NZF ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) photocatalyst was separated employing magnetic bar and afterwards, insoluble humin fraction was isolated from the reaction mixture through a filtration process. Subsequently, the unreacted ethanol and the by-product ethyl formate (EF) were individually separated using vacuum evaporation. Notably, in this process, DES facilitates the complete separation process of ethanol and EF. Finally, the main product EL, along with a small fraction of ethyl glycosides (EDGP) and 5-ethoxymethyl furfural (5EMF), was extracted using the organic solvent toluene at a temperature of 10°C, while DES was collected as a precipitate.

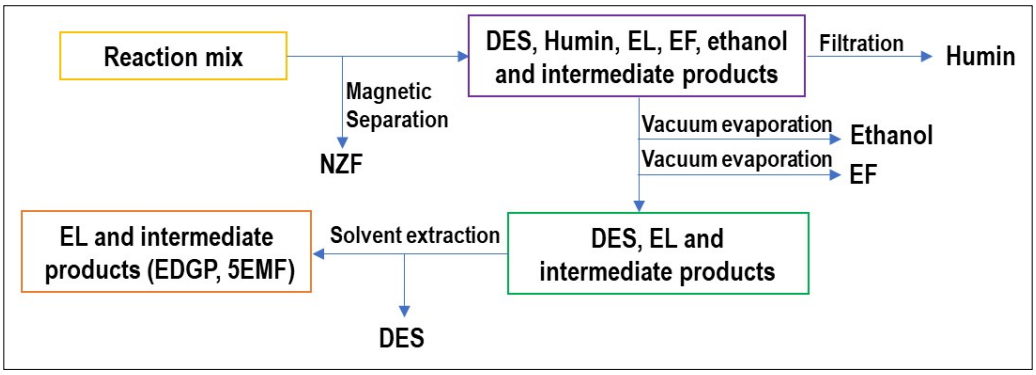

Fig. S1. Separation process of EL, DES and NZF photocatalyst

Table S2. EL-Biodiesel-Diesel blending fuel properties

Properties	EL	B10	B20	EL5B10	EL10B10	EL5B20	EL10B20
EL blending (vol %)	100	0	0	5	10	5	10
Flash point (°C)	89	71	73	74	76	78	79
Cetane number	5	49.7	51	49.2	48	47.5	46.3
Cloud point (°C)	not determined	-3	-2	-3	-4	-3	-5

Calorific value (J/g)	19146	44275	43825	43018	41762	42591	41357

[B10: 90 vol % diesel-10 vol % biodiesel; B20: 80 vol % diesel-20 vol % biodiesel; EL5B10: 95 vol % B10-5 vol % EL; EL10B10: 90 vol % B10-10 vol % EL; EL5B20: 95 vol % B20-5 vol % EL; EL10B20: 90 vol % B20-10 vol % EL]

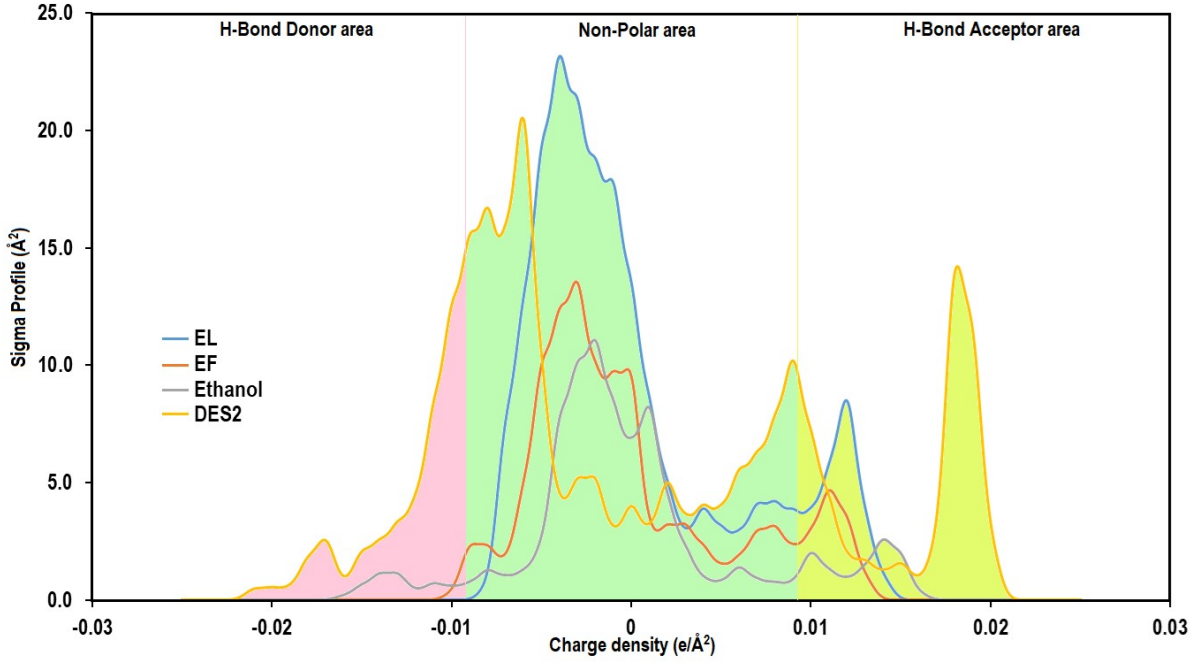

Fig. S2. Sigma profile of EL, EF, ethanol and DES2

S3. Characterization of DESs

The physical characteristics of the prepared DESs, including density, viscosity, average freezing point, and acidity were systematically assessed. Hydrometers were employed to determine density, while the average freezing points were determined by submerging the DESs in an ice bath, with a temperature sensor used to measure solvent temperatures. Viscosity measurements were conducted using an Anton Paar Viscometer SVM 3000, and pH values were determined using an Inolab pH meter.

To investigate the thermal stability of the prepared DES, TGA analysis was performed. Additionally, understanding the light absorption capacity of NZF and the complex permittivity of the DES was deemed essential in evaluating the impact of MW and visible irradiation during the EL synthesis process. The light absorption capacity of the NZF photocatalyst in DES-ethanol medium was determined through UV-VIS Spectroscopic analysis. The complex permittivity $[\varepsilon(i\omega) = \varepsilon(\omega)^{'} - i\varepsilon(\omega)^{''}]$ measurement of the DES was carried out using a dielectric probe kit and penetration depth of MW at 915 MHz frequency was determined employing Equation-S1.

$$Penetration\ depth = \frac{c}{2\pi f\sqrt{2\varepsilon^{'}[\sqrt{(1+tan^2\delta)}-1]}} \quad \text{(S1)}$$

Where c represents speed of light in free space (3 $\times$ 10^8 m/s), f represents frequency (Hz), $\varepsilon^{'}$ is relative permittivity and tan δ is dissipation factor.

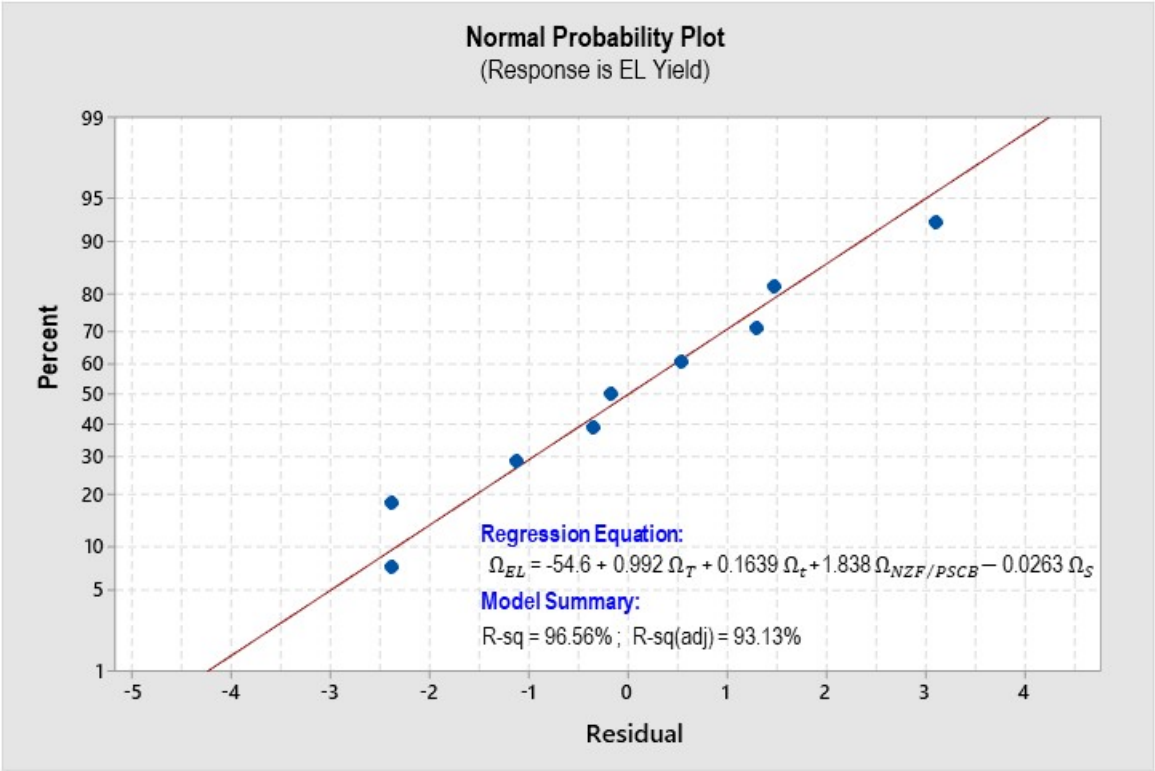

Fig. S3. Normal probability plot of residuals

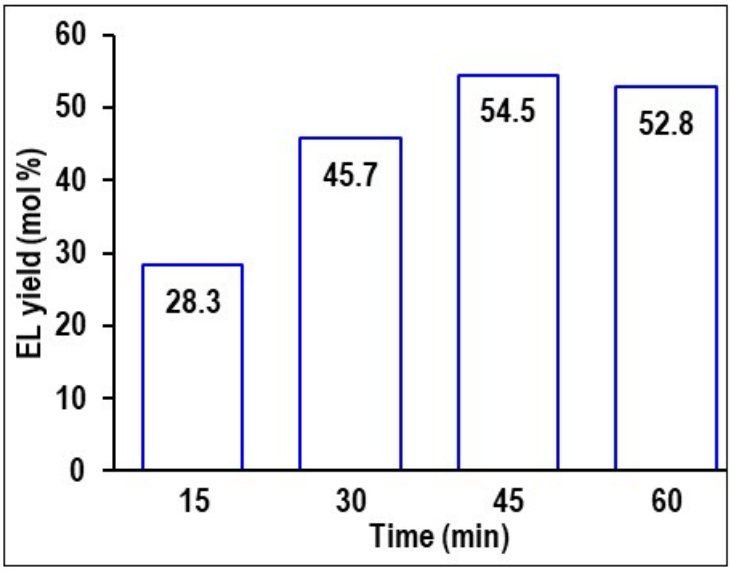

Fig. S4. Time vs EL yield in MWVIS-BR

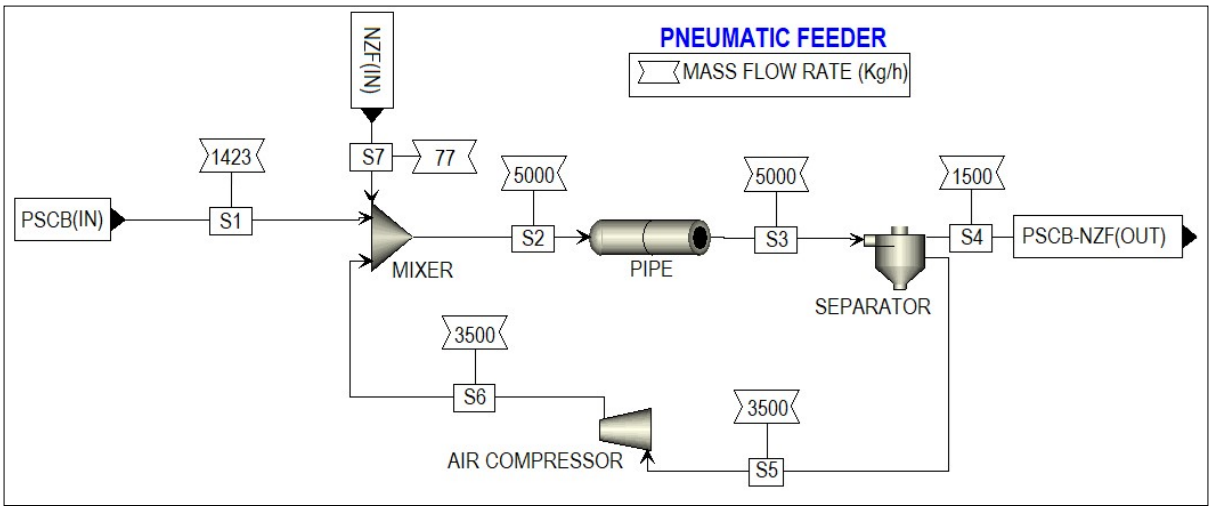

Fig. S5. Simulated process flow diagram of the PNEUMATIC FEEDER hierarchy block

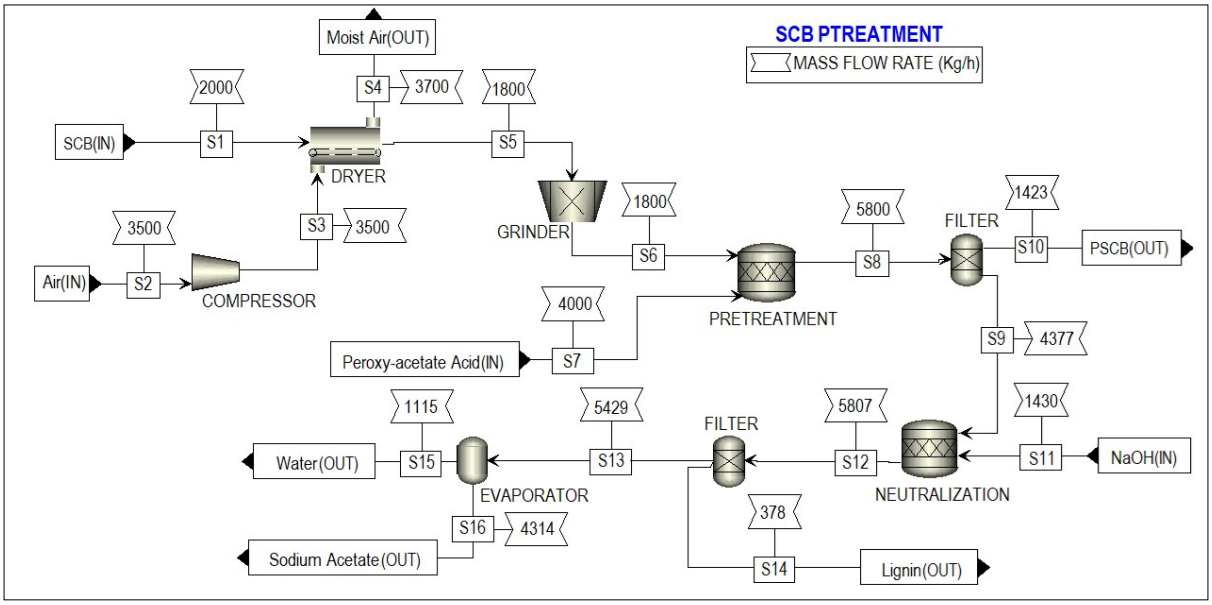

Fig. S6. Simulated process flow diagram of the SCB PRETREATMENT hierarchy block

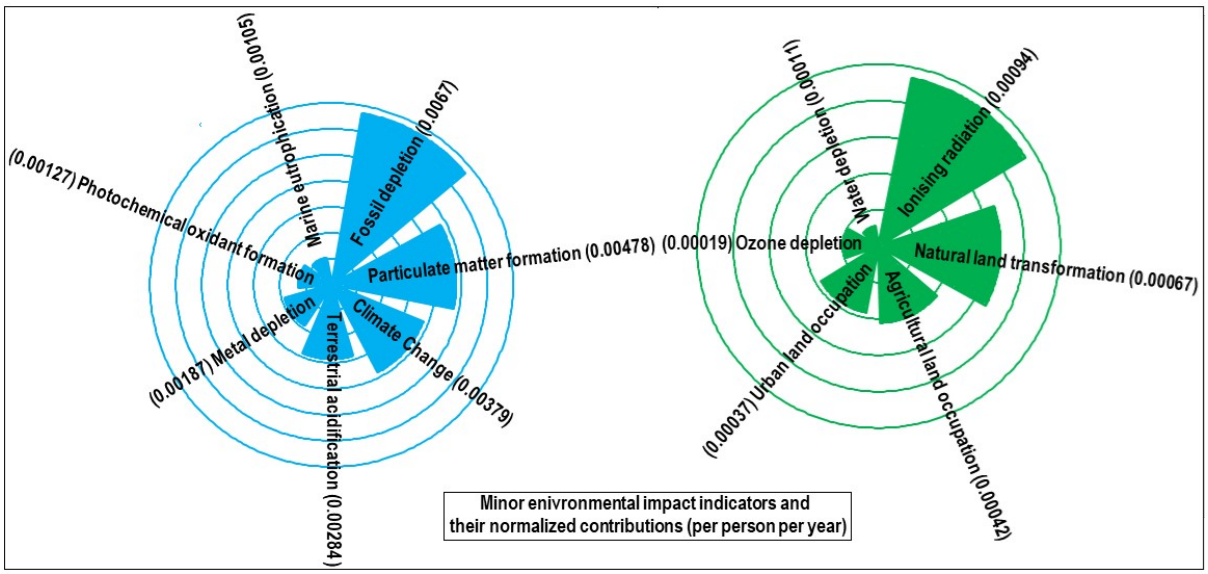

Fig. S7. minor environmental impact indicators and their normalized environmental impact contributions in SCB to EL conversion process within MWVIS-CSSR

Reference

1. C. Kundu, S.P. Samudrala, M.A. Kibria and S. Bhattacharya, Scientific Reports, 2021, **11**, 11183.
2. T. G. Ludwig and H. J. Goldberg, J. Dent. Res. 1956, **35**, 90-94.