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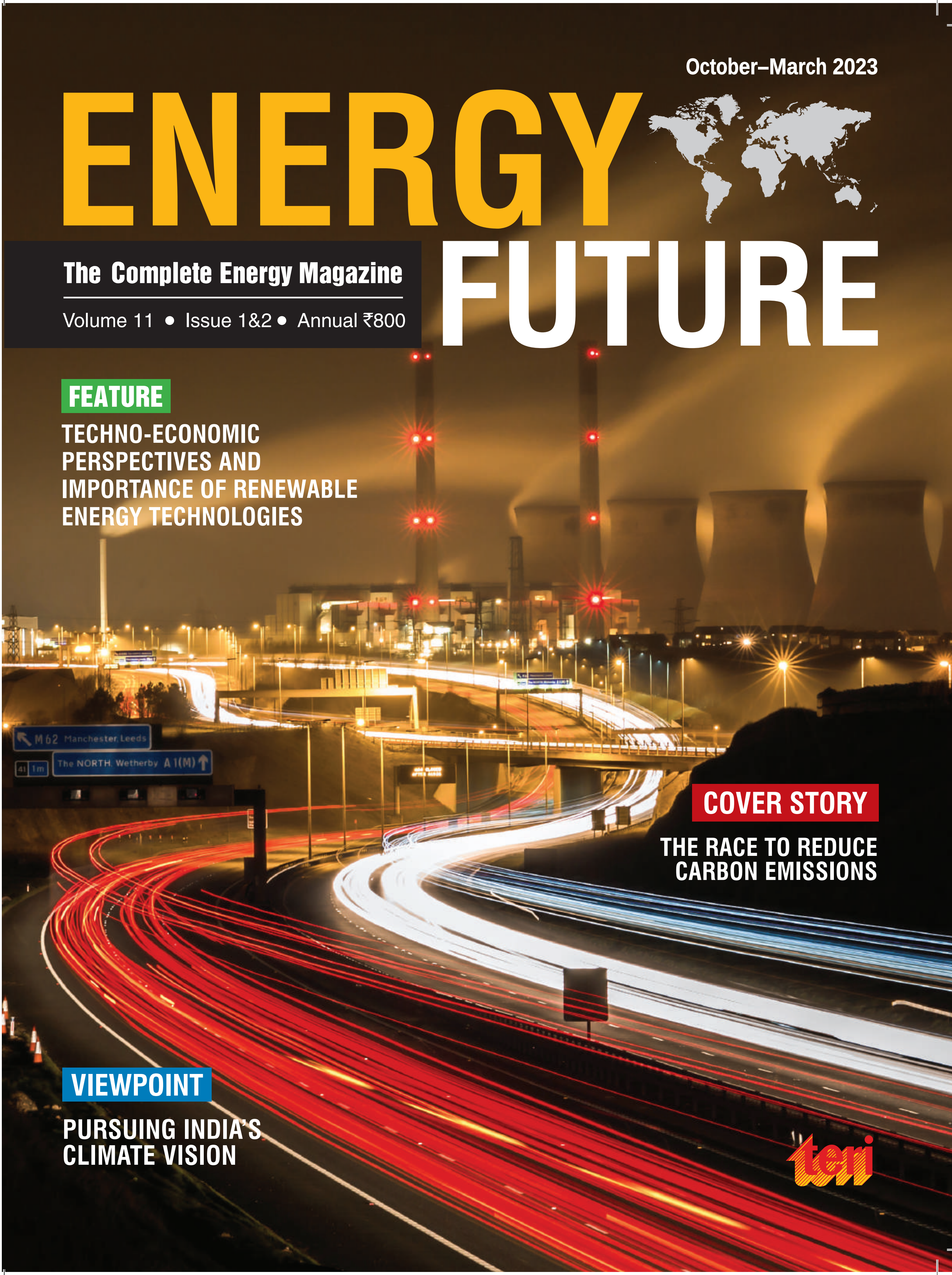

FEATURE

TECHNO-ECONOMIC PERSPECTIVES AND IMPORTANCE OF RENEWABLE ENERGY TECHNOLOGIES

COVER STORY

THE RACE TO REDUCE CARBON EMISSIONS

VIEWPOINT

PURSUING INDIA'S CLIMATE VISION

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PROSPECTS OF ETHANOL FROM AGRO-RESIDUES

Being an agrarian economy, efficient management of agricultural residues is an issue faced by numerous states across India. This article, by **T V Ramachandra** and **Deepthi Hebbale**, presents the prospects of biofuel production from agricultural residues based on the distribution of major biomass (rice and wheat) residues across the country.

For a nation, the greatest challenge of the 21st century is to cater to the growing demand for energy for transportation, heating, lighting, and industrial processes. The increased demand for fossil oil and its impacts on the environment, with greenhouse gas (GHG) emissions, have necessitated finding sustainable energy alternatives. Biofuel is emerging as a viable alternative to fossil fuels, with the potential for renewability and optimal use of biological residues. Ethanol is the most common renewable fuel being produced from biomass such as bagasse or straws. Unlike fossil fuel deposits, biomass is considered a potentially sustainable renewable resource due to its shorter period of cycling time as well as availability at decentralized levels for biofuel production and energy generation to meet the local energy demand.

Ethanol is being manufactured conventionally from first-generation feedstocks, such as sugar cane and starch-containing food crops, which pose severe challenges due to the potential threat to food and water security. Subsequent research focused on lignocellulosic biomass (second generation) feedstocks, involving the conversion of lignocellulosic polymer to ethanol through hydrolysis—which involves breakdown of the lignin-cellulose matrix and producing simple sugars such as glucose. This is followed by fermentation, the process of metabolizing glucose towards ethanol.

Research involving bio-ethanol production from lignocellulosic waste materials has included agricultural residues, forest products, municipal solid waste, industrial wastes, municipal sludge, leaf and yard waste, and a few studies involving cattle and dairy manures. Large-scale burning of agricultural residues, the consequent environmental implications in developing countries, and the need for sustainable energy alternatives, have necessitated an assessment of the potential of agriculture residues and their conversion to technically feasible and economically viable fuel.

Bio-residues in India

Agriculture is practised predominantly in India with a generation of large quantum of residues, which are partially being used as fodder, while the major fraction is being burnt or mismanaged, posing serious environmental implications. There is wide scope to convert bio-residues into bio-fuels, to cater to the burgeoning demand for liquid fuel in the industrial, agricultural, and transportation sectors. India is next to China in the production of cereals, such as rice and wheat, which have been serving as the staple source of nourishment for billions of Indians. These crops generate residues (stalk, husk, straws, etc.), which can be utilized in the unprocessed or processed form, depending on the end use. Potential uses of these residues are as animal feed, production of bioenergy, composting, or deployment in other agricultural activities, like mushroom cultivation. According to the National Policy for Management of Crop Residues (NPMCR), among the Indian states, Uttar Pradesh generates the highest crop residues (60Mt), followed by Punjab (51Mt) and Maharashtra (46 Mt). Rice and wheat contribute to nearly 70% of the crop residues (Figure 1). Among the total residue generated, the surplus residue after utilizing for various other purposes is burnt and the remains are left in the agricultural fields. According to NPMCR, approximately 92 to 100 Mt of residues are being burnt annually in India. Adverse effects of crop residue burning includes greenhouse gases (GHGs) emissions, increase in particulate matter (PM) and smog, evident from higher PM levels in Delhi due to crop residue burning in Punjab. This is 17 times more than that from all other sources,

Table 1: Crop biomass residue potential in India

Crop group	Crop	Growing season	Residue	Gross potential (Mt)	Surplus potential (Mt)	Residue available for 1 kg of crop
Cereal	Rice	Kharif, Rabi, Summer	Straw	154	43.5	1.5
			Husk			0.2
	Wheat	Rabi	Stalk	131.1	28.4	1.5
			Pod			0.3

*Note – **Kharif**: From June/July–October, **Rabi**: From October/November–March/April, **Zaid/Summer**: From April-June*

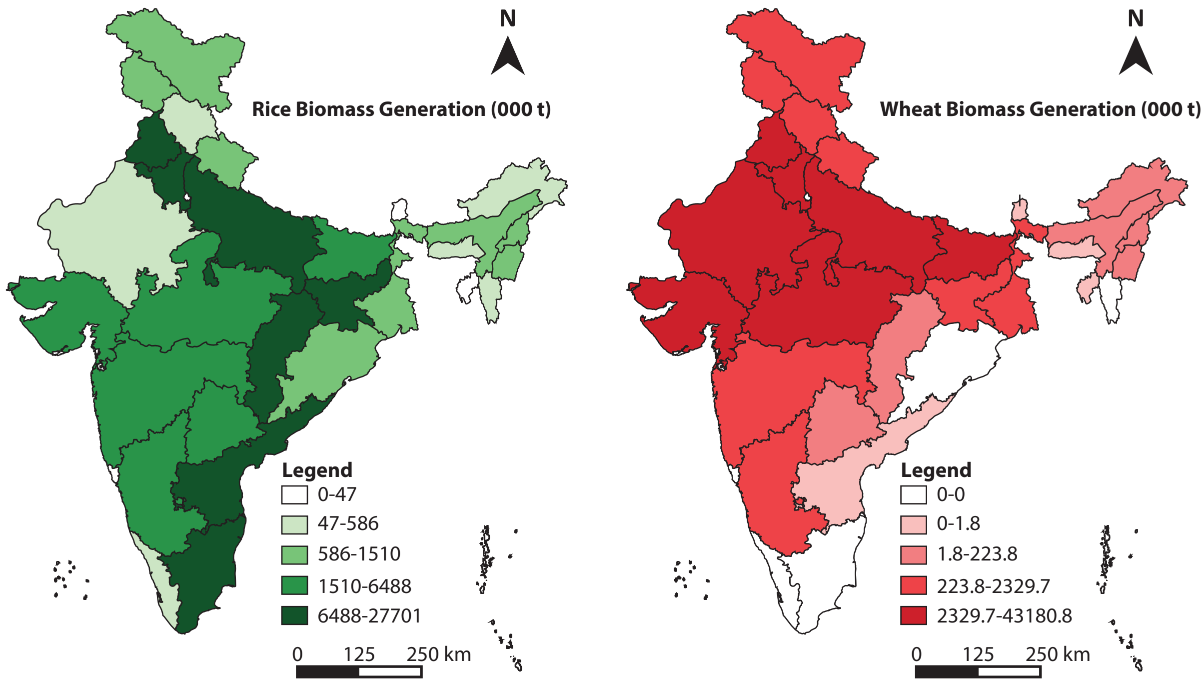

Figure 1: Representation of paddy and wheat-producing states across India

such as garbage burning, industries, and vehicle emissionsthe second largest agro-based economy with year-round crop cultivation, generates a large amount of agricultural waste, including crop residues. In the absence of adequate sustainable management practices, approximately 92 seems a very small number of metric tonnes of crop waste is burned every year in India, causing excessive particulate matter emissions and air pollution. Crop residue burning has become a major environmental problem causing health issues as well as contributing to global warming. Composting, biochar production and mechanization are a few effective sustainable techniques that can help to curtail the issue while retaining the nutrients present in the crop residue in the soil. The government of India has attempted to curtail this problem, through numerous measures and campaigns designed to promote sustainable management methods such as converting crop residue into energy. However, the alarming rise of air pollution levels caused by crop residue burning in the city of Delhi and other northern areas in India observed in recent years, especially in and after the year of 2015, suggest that the issues is not yet under control. The solution to crop residue burning lies in the effective implementation of sustainable management practices with Government interventions and policies. This manuscript addresses the underlying technical as well as policy issues that has prevented India from achieving a long-lasting solution and also potential solutions that have been overlooked. However, effective implementation of these techniques also requires us to look at other socioeconomic aspects that had not been considered. This manuscript also discusses some of the policy considerations and functionality based on the analyses and current practices. The agricultural waste sector can benefit immensely from some of the examples from other waste sectors such as the municipal solid waste (MSW). These crop residues are composed of cellulose, lignin, and hemicellulose, which serves as ideal raw material for biofuel production.

National Biofuel Policy

The share of road transport is around 6.7% of India's Gross Domestic Product (GDP), of which diesel makes up about 72% and petrol 23%. In India, domestic crude oil production only meets about 17.9% of the demand, the rest is sufficed by importing crude oil. This vulnerable status of India needs to change with the utilization of alternative fuels produced from indigenous renewable feedstock. The government of India has undertaken multiple interventions to promote biofuel production and blending of bioethanol with petroleum, as well as reducing import by 10% in 2022 (India, 2018). In this regard, the National Biofuel Coordination Committee (NBCC), recently constituted under the National Policy on Biofuels, has allowed the production of ethanol from maize and surplus rice available from the Food Corporation of India (FCI). This has been done by involving public sector oil marketing companies (OMCs), such as IOCL, BPCL, and HPCL under the ethanol blended petrol (EBP) programme.

Large-scale bioethanol production in the country can be taken forward with the establishment of a transparent framework of policy, mandates, and subsidies that dwell on the production of biofuels using various conversion technologies and promoting utilization of locally available feedstocks—generated in large quantities in the agri-states of India.

Production of bioethanol from bio-residues: Production of bioethanol entails three main processes, namely:

i. pretreatment of raw materials to break down recalcitrant lignocellulose structure;
ii. enzymatic hydrolysis of polysaccharides (e.g., cellulose and hemicellulose) to release simple sugars; and
iii. fermentation of these simple sugars to bioethanol (Figure 2).

A major limitation to commercializing bioethanol production using lignocellulosic biomass is the presence of a complex assembly of polymers, such as cellulose, hemicelluloses, and lignin that are naturally recalcitrant to enzymatic conversion. Pretreatment to break the recalcitrant structure is crucial to make cellulose accessible to enzymatic saccharification. Assessment of the biochemical composition of lignocellulosic biomass aids in developing appropriate pre-treatment technologies for the deconstruction of rigid structure and in selecting enzymes to release the fermentable sugars for bioethanol production.

During hydrolysis, lignocellulosic biomass is broken down into several compounds other than glucose, such as weak acids, furans, and phenolic compounds, which are inhibitors in the fermentation process. Alkali pretreatments using NaOH, KOH, CaOH, and Na_2CO_3 are being widely applied for the removal of lignin from lignocellulosic biomass due to the efficient removal of ester bonds between lignin, hemicellulose, and cellulose. Fermentation of lignocellulosic biomass is carried out using the strain of *Saccharomyces cerevisiae*. But, this strain is unable to ferment inhibitor compounds, which are generated during the hydrolysis step. Detoxification of these inhibitory compounds is performed by extraction with ether or ethyl acetate and treatment with alkali or sulfite. Also, using enzymes extracted from either ligninolytic or cellulolytic fungi, or bacteria for hydrolysis would circumvent the detoxification step. Cellulolytic enzymes play a vital role in the degradation of lignocellulosic biomass and these enzymes have been employed in industries to produce fermentable sugars. Fungal cellulases are most employed as they are inducible enzymes excreting into the environment.

This article presents the prospects of biofuel from agriculture residues based on the distribution of major biomass (rice and wheat) residues across India, which is an important factor in assessing the feasibility of plant installation for bioethanol production and discusses the challenges in the technology so far. Bioethanol production from rice and wheat straw is feasible using marine cellulolytic bacteria for hydrolysis and isolated yeast strain *Pichia kudriavzevii* for fermentation.

Methods

- **Feedstock (lignocellulosic residues):** Dried paddy and wheat straw were dried at 50–60°C for 15 to 20 minutes, pulverized using a grinder, and then sieved to get powder of < 0.1mm. These samples were stored in air-tight zip lock covers for further analysis.
- **Pretreatment of feedstock (bio-residues):** Dilute acid pretreatment was carried out using 2% H_2SO_4 for 10 g of straw and autoclaved at 121°C for 45 minutes. After pretreatment, the biomass was washed with distilled water and subjected to simultaneous saccharification and fermentation (SSF).
- **Fermentation of bio-residues:** Saccharification was carried out using *Vibrio parahaemolyticus* isolated from marine source exhibiting higher cellulolytic activity. Yeast strain *Pichia kudriavzevii*, isolated from toddy strain exhibiting thermotolerance, was selected for fermentation. SSF was carried out at 55°C, 100 rpm for 24 hours. Reducing sugar after hydrolysis was estimated using DNS method. The ethanol present in the fermented broth was analysed using GC-FID (gas chromatography with flame ionization detection).
- **SEM** (scanning electron microscope) **analysis:** Lignocellulosic biomass surface morphology (untreated, acid-treated, and enzyme-treated biomass) was qualitatively analysed using SEM (JEOL-IT 300). Pulverized straw samples were placed on an aluminium

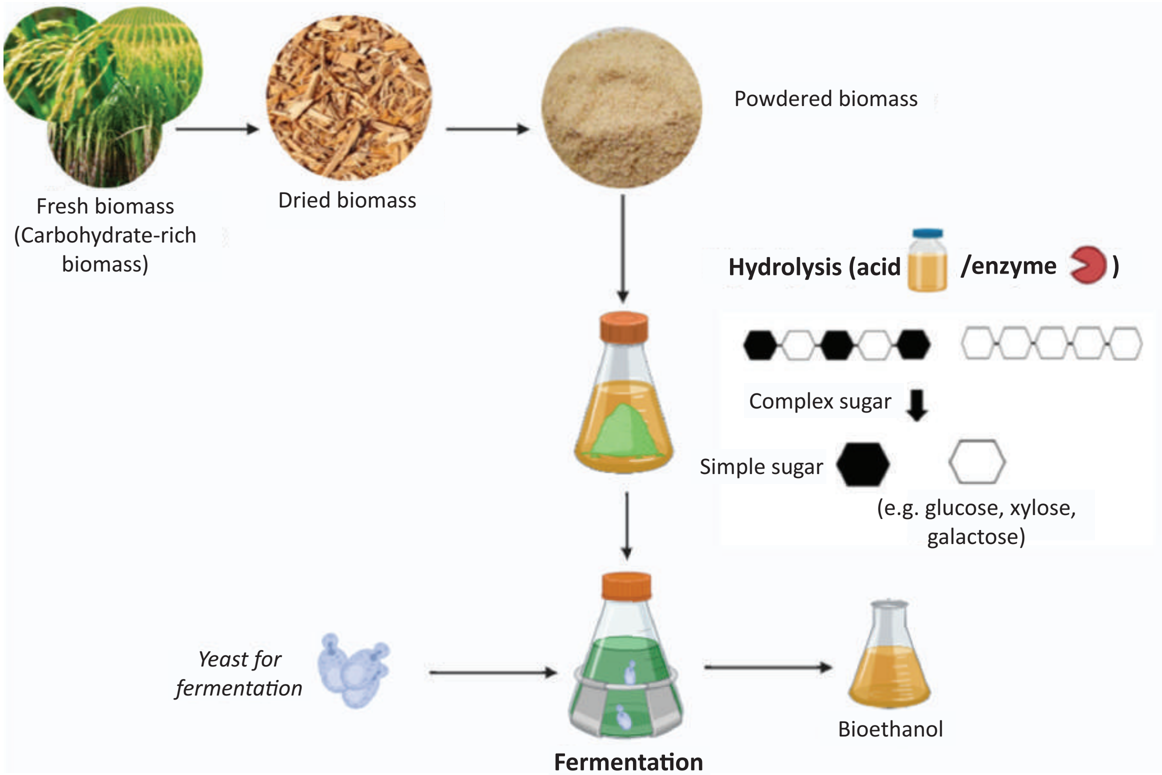

Figure 2: Schematic representation of bioethanol production using lignocellulosic biomass

specimen mount using conductive carbon tape. Sputter gold coating was performed to prevent charging. Samples were then examined in SEM under vacuum conditions at an accelerating voltage of 10 kV.

Results and Discussions

- **Lignocellulosic residue:** Key factor in bioethanol production from lignocellulosic biomass is its chemical composition. The composition of lignocellulosic biomass is variable base on their environmental conditions and interactions. The biochemical composition of rice and wheat straws is listed in Table 1. Major components of these residues (paddy and wheat straw) are lignin $[C_9H_{10}O_3(OCH_3)_{0.9\text{-}1.7}]_n$, cellulose $(C_6H_{10}O_5)_x$, and hemicellulose $(C_5H_8O_4)_m$. with the relative share of about 18.81%, 36%, and 19%, respectively. Cellulose is mostly composed on glucose subunits that are linked linearly by hydrogen bonding. Rigidity to the residue is imparted by the number of additional hydrogen bonds and also the orientation of linkages.
- **Bioethanol from lignocellulosic residue:** Simultaneous saccharification and fermentation of feedstock (paddy and wheat straw) was carried out by taking 10 g of biomass. Biomass was subjected to 2% H_2SO_4, and the pre-treated biomass was hydrolysed using V. parahaemolyticus. It was simultaneously saccharified using yeast strain P. kudriavzevii. Paddy straw produced 0.28 g/g of ethanol (36.7 L/100 kg) with a conversion efficiency of 76.62%, and wheat straw produced 0.42 g/g of ethanol (53.73L/100 kg) with a conversion efficiency of 64.82%. Lower ethanol production from rice straw is due to high silica content compared with other lignocelluloses. The presence of silica in the outer layer of rice straw reduces enzymatic hydrolysis and ethanol production yield. In order to improve the ethanol yield from rice straw, alkali treatment is carried out using sodium carbonate. It was seen that this pre-treatment was efficient (>91%) in removing silica from the straw. Subjecting rice straw to acid pre-treatment with ultrasound and subsequent enzyme hydrolysis using enzyme extracted from T. reesei, obtained ethanol of 11g/L after 7 days of fermentation with S. cerevisiae. Subjecting rice straw to subcritical water treatment and enzyme hydrolysis obtained ethanol of 0.011g/g (1.39L/100 kg). Lower ethanol yield in this study is due to utilization of non-domesticated strain for hydrolysis as well as fermentation. However, good ethanol is produced in a shorter period than other studies, which can be further improved by selecting strains with specific characteristics, through hybridization or evolutionary engineering techniques.
- **Effect of pre-treatment on straw morphology:** SEM images were taken to investigate the lignocellulose

morphology, structures, and characterization at the nanoscale. SEM images of untreated and acid-treated biomass were compared, untreated biomass had a smooth surface, whereas the acid-treated biomass indicated loosened structures exposing the cellulose structures for enzyme hydrolysis.

» **Bioethanol prospects from agricultural residues in India**: Tables 2 and 3 indicate the availability, seasonality, total and surplus biomass production of rice and wheat along with its bioethanol potential across states in India. Higher quantity of bioethanol potential is directly proportional to the large quantity of biomass generated by the state. However, a major challenge is the dispersed nature of agriculture residue availability, which necessitates setting up mobile biorefineries or biorefineries at disaggregated levels.

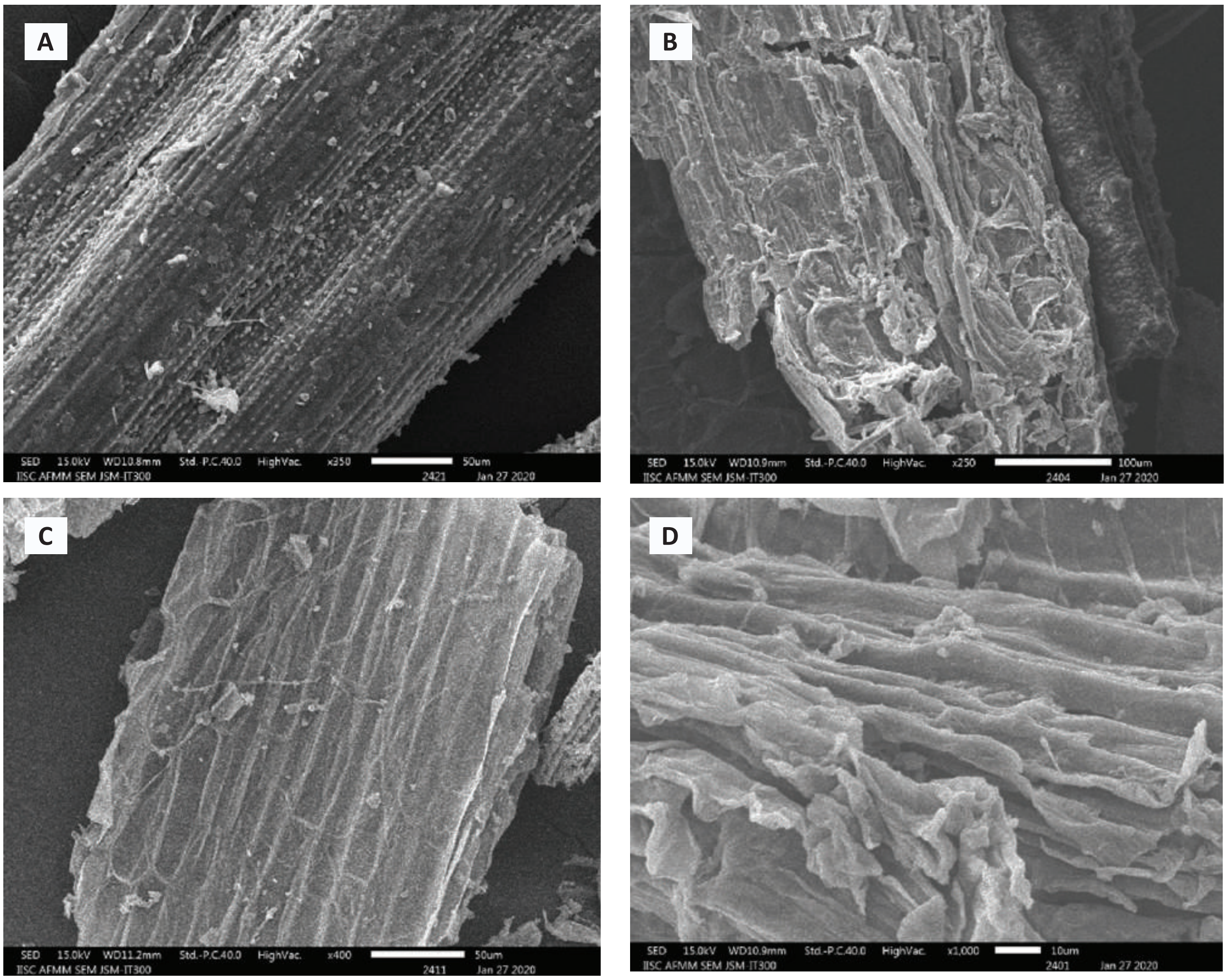

Figure 3: Scanning electron microscopy images of paddy straw; **A**: Untreated, **B:** Acid treated and wheat straw; **C**: Untreated, **D:** Acid treated

Table 2: Biochemical composition of selected biomass residue

Biomass residue	Carbohydrates (per 100g)		Fat (g)	Proteins (g)	Water	Energy (kJ)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
	Sugar (g)	Dietary fibre (g)								
Paddy straw	0.05	0.4	0.28	2.6	68.44	540	36	19	18.81	11.88
Wheat straw	0.41	12.2	1.54	12.61	13.1	1368	36.6	18.9	16.2	6.6

Table 3: State/UT-wise availability, seasonality, total, and surplus biomass production of rice along with its bioethanol potential

States/UT	Availability	Seasons	Total production (000 t)	Surplus production (000 t)	Bioethanol potential (million L)
Andaman & Nicobar Islands	+	Kharif, Rabi, early Kharif	33.46	33.46	0.45
Andhra Pradesh	+	Kharif, Rabi, early Kharif	16925.74	9360.01	367.3
Arunachal Pradesh	+	Kharif	35.78	356.78	9.68
Assam	+	Kharif, Rabi, early Kharif	10484.05	651.28	310.89
Bihar	+	Kharif, Rabi, early Kharif	15035.21	1672.26	833.82
Chandigarh	+	Kharif	0.21	0.21	0
Chhattisgarh	+	Kharif	14759.48	14759.48	400.37
Dadra & Nagar Haveli	+	Kharif	48.18	47.01	0.65
Daman & Diu	+	Kharif	4.69	4.69	0.06
Delhi			0	0	0
Goa	+	Kharif, Rabi	248.33	162.4	17.51
Gujarat	+	Kharif	3156.28	2891.88	256.85
Haryana	+	Kharif	7733.03	7733.03	500.65
Himachal Pradesh	+	Kharif	262.43	262.43	42.71
Jammu & Kashmir	+	Kharif	711.71	711.71	19.31
Jharkhand	+	Kharif	7488.94	7488.94	406.29
Karnataka	+	Kharif, Rabi, early Kharif	8315.67	6272.04	113.16
Kerala	+	Kharif, Rabi, early Kharif	1090.07	332.6	25.39
Lakshadweep			0	0	0
Madhya Pradesh	+	Kharif	5776.53	5776.53	156.52
Maharashtra	+	Kharif	6200.23	6200.23	168.18
Manipur	+	Kharif	994.58	994.58	174.48
Meghalaya	+	Kharif	201.64	122.02	16.41
Mizoram	+	Kharif	122.03	120.26	16.36
Nagaland	+	Kharif	857.59	839.76	23.26
Odisha	+	Kharif, Rabi, early Kharif	15502.85	1509.52	540.24
Puducherry	+	Kharif, Rabi, early Kharif	74.77	25.18	1.01
Punjab	+	Kharif	23067.68	23067.68	4599.73
Rajasthan	+	Kharif	586.46	586.46	0
Sikkim	+	Kharif, Rabi	42.38	42.38	1.15
Tamil Nadu	**+**	**Kharif, early Kharif**	**12598.97**	**12598.97**	**341.76**
Telangana	+	Kharif	11429.93	6488.25	248.04
Tripura	+	Kahrif	1786.33	1786.33	38.76
Uttar Pradesh	+	Kharif	27701.21	27701.21	2037.99
Uttarakhand	+	Kharif	1240.69	1137.36	50.48
West Bengal	+	Kharif, Rabi	30648.82	1024.15	297.35
All-India			225165.95	142761.08	12016.81

Data source: National Food Security Mission: https://nfsm.gov.in/dbt/admin/login.aspx

Table 4: State-wise availability, seasonality, total, and surplus biomass production of wheat along with its bioethanol potential

States	Availability	Seasons	Total production (000 t)	Surplus production (000 t)	Bioethanol potential (million L)
Andaman & Nicobar			0	0	0
Andhra Pradesh		Rabi	0.85	0	0
Arunachal Pradesh	+	Kharif	9.48	0.94	0.26
Assam	+	Kharif, Rabi	65.38	3.24	0.89
Bihar	+	Kharif, Rabi	8038.65	824.36	227.52
Chandigarh	+		3.9	0	0
Chhattisgarh	+	Kharif	223.78	44.31	12.23
Dadar & Nagar Haveli			0	0	0
Daman & Diu			0	0	0
Delhi			0	0	0
Goa			0	0	0
Gujarat	+	Kharif, Rabi	5570.24	1654.36	456.6
Haryana	+	Kharif, Rabi	1765.3	1469.98	405.71
Himachal Pradesh	+	Kharif, Rabi	919.88	182.14	50.27
Jammu & Kashmir	+	Kharif, Rabi	695.01	68.81	18.99
Jharkhand	+	Kharif	370.73	18.35	5.06
Karnataka	+	Kharif, Rabi	344.15	27.26	7.52
Kerala			0	0	0
Lakshadweep			0	0	0
Madhya Pradesh	+	Kharif, Rabi	22371.73	4500.38	1242.1
Maharashtra	+	Kharif, Rabi	2329.71	691.92	190.97
Manipur	+	Kharif	8.32	0.41	0.11
Meghalaya	+	Kharif	0.83	0.04	0.01
Mizoram		Kharif	0	0	0
Nagaland	+	Kharif	8.39	0	0
Odisha		Kharif, Rabi	0	0	0
Puducherry			0	0	0
Punjab	+	Kharif, Rabi	25446.21	9374.75	2587.43
Rajasthan	+	Kharif, Rabi	15617	0	0
Sikkim	+	Kharif, Rabi	1.84	0.18	0.05
Tamil Nadu			0	0	0
Telangana	+	Rabi	15.26	0	0
Tripura	+	Rabi	0.91	0.03	0.01
Uttar Pradesh	+	Kharif, Rabi	43180.76	6021.02	1661.8
Uttarakhand	+	Rabi	1222.25	121	33.4
West Bengal	+	Kharif, Rabi	1349.49	66.8	18.44
All India			129560.05	25070.28	6919.37

Data source: National Food Security Mission https://nfsm.gov.in/dbt/admin/login.aspx

Table 5: Simultaneous saccharification and fermentation of lignocellulosic bio-residue

Feed-stocks	Biomass (g)	Acid pre-treatment	Enzyme hydrolysis	Fermentation	Initial sugar (g)	Final sugar (g)	Fermented sugar (g)	Ethanol (g)	Theoretical yield	Conversion efficiency (%)
Paddy straw	10	2% H_2SO_4, 121°C for 45 min	*V. paraheamolyticus*, 55°C 100 rpm for 24 h	*Pichia kudriavzevii* (35°C, 100 rpm for 72 h)	8.12	0.75	7.37	2.88	3.76	76.62
Wheat straw					13.8	0.98	12.82	4.24	6.54	64.85

Conclusion

Increased fossil fuel demand, coupled with the dwindling stock and concerns of global warming, has necessitated the exploration of environmentally sustainable, renewable, and economically viable alternatives to cater to the growing demand for liquid fuel in the transportation and industries sectors. The availability of abundant residues of rice (43.86 Mt) and wheat (25.07 Mt) in India demands for their sustainable utilization in the production of bioethanol. India produces large quantities of rice and wheat residues; bioconversion of these residues into biofuels will aid in prudent waste management by minimizing instances of stubble burning. The prospects of utilizing marine bacterial strain *V. parahaemolyticus* for enzyme hydrolysis and yeast strain *P. kudriavzevii* for fermentation is explored in the bioethanol production process. Simultaneous saccharification and fermentation of paddy straw produced 0.28 g/g of ethanol with a conversion efficiency of 76.62%. Similarly, the simultaneous saccharification and fermentation of wheat straw produced 0.42 g/g of ethanol with a conversion efficiency of 64.82%.

The study highlights that biofuel production from lignocellulosic biomass is eco-friendly and cost-effective, considering the need for energy and environmental security. It facilitates the optimal use of agro-wastes, as of now being burnt in most parts of Asian countries and contributing to air pollution and the associated health impacts. Utilization of paddy and wheat straw will likely produce ethanol of 30-60 L per 100 kg of biomass. The surplus biomass residue generation in every state and its bioethanol production potential helps in evolving appropriate strategies for operationalizing biofuel production units across India. Utilizing the hitherto wasted abundant resources of bio-residues for valuable products is quintessential for lowering the carbon footprint associated with its mismanagement. EF

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