# **Chapter 8 Perspectives of Agro-Waste Biorefineries for Sustainable Biofuels**



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**M. S. Dhanya**

# **8.1 Introduction**

The global production of crop residues throughout the year is in surplus quantity, but the major portion has been remained unutilized (Prasad et al. [2020;](#page-22-0) Kosre et al. [2021;](#page-19-0) Singh et al. [2020\)](#page-23-0). The judicious management of the agro-residues is very much needed to address associated environmental and health concerns (Chen et al. [2020;](#page-16-0) Sharma et al. [2020a;](#page-23-1) Klai et al. [2021\)](#page-19-1). The immense potential of biomass residues for various purposes are well-documented (Prasad et al. [2020;](#page-22-0) Daioglou et al. [2016;](#page-16-1) Honorato-Salazar and Sadhukhan [2020;](#page-18-0) Xu et al. [2020;](#page-24-0) Venkatramanan et al. [2021a\)](#page-24-1). The biomass wastes generated from agriculture sector is mainly from post harvesting of crops and post processing (Sadh et al. [2018\)](#page-23-2). The abundance, renewability, biodegradability and inexpensiveness make the agricultural crop wastes and agro-processing wastes as a viable feedstock for eco-friendly and sustainable products (Nguyen [2017;](#page-21-0) Duque-Acevedo et al. [2020;](#page-17-0) Ibitoye et al. [2021\)](#page-18-1). The biorefineries based on agro-residues were reported by many researchers (Serna-Loaiza et al. [2018;](#page-23-3) Fito et al. [2019;](#page-17-1) El-Ramady et al. [2020;](#page-17-2) Redondo-Gómez et al. [2020\)](#page-23-4).

The major lignocellulosic crop residues in Asia are generated from rice, wheat and maize, in Europe and North America are from wheat and maize respectively (Kim and Dale [2004;](#page-19-2) Sharma et al. [2020b\)](#page-23-5). The major residues generated from the crop harvesting are husk, straw, leaves and stalks (Deshwal et al. [2021\)](#page-16-2). The agricultural processing has also added to agro-residue production by means of husk, hull, shell, bagasse and fibres (Go et al. [2019\)](#page-17-3). The small intervals between harvesting of one crop and sowing of next crop, lack of land for post harvesting and post processing crop residue disposal, long time required for biodegradation and less suitability as fodder exert pressure on farmers to choose more easier method of open burning of

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<sup>©</sup> The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2022 Y. K. Nandabalan et al. (eds.), *Zero Waste Biorefinery*, Energy, Environment, and Sustainability, [https://doi.org/10.1007/978-981-16-8682-5\\_8](https://doi.org/10.1007/978-981-16-8682-5_8)

crop residues (Pandiyan et al. [2019;](#page-22-1) Dai et al. [2020\)](#page-16-3). The effective and sustainable utilization of agro-residues is urgently required to reduce the impacts of open burning and emissions of Greenhouse gases from open dumping (Bhardwaj et al. [2019;](#page-15-0) Prasad et al. [2020\)](#page-22-0). The developing countries are more benefitted from the use of agroresidues with improved air quality and ensured energy security (Ullah et al. [2015;](#page-24-2) Naqvi et al. [2020\)](#page-21-1). These secondary feedstock at the harvesting or processing site saves transportation and handling cost compared to first generation raw materials making it a more potential candidate for production of bioenergy and biochemicals (Hassan et al. [2019;](#page-17-4) Raud et al. [2019;](#page-23-6) Kumar et al. [2020a\)](#page-19-3). The development of effective biorefinery approach with technologies enable the agrarian countries rich in agricultural residues to achieve food and fuel sustainability (Nanda et al. [2015;](#page-21-2) Solarte-Toro and Alzate [2021\)](#page-24-3). This chapter aimed at the perspectives and challenges of agro-residues for biorefinery of biofuels and biochemicals with main focus on India with different production techniques.

# **8.2 Second Generation Lignocellulosic Biorefinery**

The conflict on food-fuel made the focus stronger on the second generation biorefineries over the biorefineries depend on first generation feedstock (Sadhukhan et al. [2018;](#page-23-7) Olguin-Maciel et al. [2020;](#page-21-3) Patel and Shah [2021\)](#page-22-2). India being an agrarian country huge scope lies in the utilization of lignocellulosic agro-wastes for biorefinery (Banu et al. [2021;](#page-15-1) Govil et al. [2020\)](#page-17-5). The estimated crop residue production in our country as per Ministry of New and Renewable Energy is around 500 million tonnes with more than 60% from rice, wheat, sugarcane and cotton (MNRE [2014\)](#page-21-4). The annual surplus of biomass available for bioenergy production was 34% of the total crop residue generation with of 234 MT (Hiloidhari et al. [2014\)](#page-17-6). The crop residue production varies with the states in India with Uttar Pradesh at topmost position (NPMCR [2014\)](#page-21-5).

The lignocellulosic residues produced from crops after harvesting and conversion to various products by processing in India is given in Fig. [8.1.](#page-1-0) The major wastes produced after the post harvesting of crops are straw or stalks, for the cereals, pulses

<span id="page-1-0"></span>

and oilseed crops. The post-processing of crops had generated residues such as husk, bagasse and pressed cakes. Hiloidhari et al. [\(2014\)](#page-17-6) estimated the bioenergy potential of 26 crops cultivated in India from its 39 residues. Chowdhury et al. [\(2018\)](#page-16-4) evaluated the scope of straw and husk of rice, straw of wheat, press cakes of oilseeds, bagasse from sugarcane, coconut shells, pseudo-stem of banana and banana peels for second generation biorefineries. The bioethanol production potential of 5.42 billion litres were reported from the straw of rice, wheat and maize and bagasse of sugarcane with its 50% conversion efficiency and estimated as surplus to meet 10% bioethanol blending (Sukumaran et al. [2010\)](#page-24-4).

The Fig [8.2](#page-3-0) shows common lignocellulosic residues generated from major crops in India after harvesting and processing. The leaves, stalk, husk, fruit bunches and vegetable peels have low economic value but has immense potential for production of various value-added products (Sadh et al. [2018;](#page-23-2) Kumar and Yaashikaa [2020;](#page-19-4) Molina-Guerrero et al. [2020;](#page-21-7) Jusakulvijit et al. [2021\)](#page-18-2).

The integrated approach based biorefineries for the utilization of agro-wastes for biofuels, bioenergy, and other high-value chemicals have been needed for sustainable development (López-Molina et al. [2020;](#page-20-0) Philippini et al. [2020;](#page-22-3) Leong et al. [2021\)](#page-20-1).

### **8.3 Composition of Agro-Residues**

The constituents of agro-residues play an important role in biorefinery for biofuel and biochemical production. The major components of these lignocellulosic wastes are cellulose, hemicellulose (xyloglucan, rhamnogalactan or glucurono-arabinoxylan), lignin, proteins, sugars soluble in water, resins and pigments soluble in ethers and alcohols (Kumar et al. [2020b;](#page-19-5) Rishikesh et al. [2021;](#page-23-8) Šelo et al. [2021\)](#page-23-9). The structural components of agro-residues differ depending on genetic and environmental factors (Kosre et al. [2021;](#page-19-0) Paschos et al. [2020\)](#page-22-4). These lignocellulosic materials (Fig. [8.1\)](#page-1-0) had major fraction of cellulose followed by hemicellulose and lignin (Fig. [8.3\)](#page-4-0). The cellulosic micro-fibrils in bundles provide cell wall strength and flexibility which was covered by resistant lignin with hemicellulose in between (Berglund et al. [2020\)](#page-15-2).

The agro-residues had 25–50% of cellulose, with its monomer glucose having β-1, 4 linkage (Rishikesh et al. [2021;](#page-23-8) Bhatnagar et al. [2020;](#page-15-3) Lojkova et al. [2020\)](#page-20-2); 15–35% of hemicellulose, a heteropolysaccharide contains D-glucose, D-xylose, D-galactose, D-mannose and L-arabinose (Kumla et al. [2020;](#page-19-6) Huang et al. [2021;](#page-18-3) Liu et al. [2021\)](#page-20-3) and 12–20% of lignin consists of phenolic biopolymer with 4 hydroxyphenyl, guaiacyl, and syringyl subunits (De et al. [2020;](#page-16-5) Domínguez-Robles et al. [2021\)](#page-16-6). The structural composition of residues from major crops and after processing are compiled from Gupte and Madamwar [\(1997\)](#page-17-7); Prasad et al. [\(2007\)](#page-22-5); Furlan et al. [\(2012\)](#page-17-8); Kumar et al. [\(2018a\)](#page-19-7); Nasir et al. [\(2019\)](#page-21-8); Ibarra-Díaz et al. [\(2020\)](#page-18-4); Kumar et al. [\(2020b\)](#page-19-5) and summarized in Table [8.1.](#page-4-1)



<span id="page-3-0"></span>**Fig. 8.2** Lignocellulosic residues from major crops in India after harvesting and processing (Singh and Gu [2010;](#page-23-10) Kumar et al. [2015;](#page-19-8) López-Molina et al. [2020\)](#page-20-0)

# **8.4 Environmental Benefits of Second Generation Biorefinery from Agro-Residues**

The fossil fuel burning and biomass burning are major anthropogenic contributors to air pollution, climate change and global warming (IPCC [2018;](#page-18-5) Bhattacharyya and Barman [2018;](#page-15-4) Fagodiya et al. [2019;](#page-17-9) Kaushal and Prashar [2021\)](#page-19-9). The emissions

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**Fig. 8.3** Major constituents of agro-residues

#### **THEORY COMPOSITION OF**<br>common agricultural residues Agro-residues Cellulose (%) Hemicellulose (%) Lignin  $(\%)$ Rice straw 26–40 18–28 12–14 Wheat straw  $\begin{array}{|l} 33-41 \\ 20-32 \\ 13-20 \\ \end{array}$ Maize stover  $38-40$  28 7–21 Barley straw 31–45 27–38 14–19 Nut shells  $\begin{array}{|l|l|} 25-30 & 25-30 \end{array}$  | 30–40 Sorghum straw  $\begin{array}{|l} 32 \end{array}$   $\begin{array}{|l} 24 \end{array}$  13 Bagasse from sugarcane 39 37 21 Bagasse from Sweet sorghum 34–45 18–28 14–22 Rice husk  $35-40$  15–20  $20-25$ Rice bran  $34$  28.2 24.8 Corn cobs  $\begin{array}{|l|}45 \end{array}$   $\begin{array}{|l|}35 \end{array}$  15 Wheat husk  $\begin{array}{|l|l|} 36 & 18 & 16 \end{array}$ Rye husk  $\begin{array}{|l|l|} 26 & 16 \end{array}$  13

<span id="page-4-1"></span><span id="page-4-0"></span>**Table 8.1** Composition of

of methane and nitrous oxide from crop residue burning in India during 2017–18 were 176.1 Tg and 313.9 Gg of  $CO<sub>2</sub>$  and  $CH<sub>4</sub>$  respectively (Venkatramanan et al. [2021b\)](#page-24-5). The open biomass burning contributes to around 40% of total emissions of carbon dioxide and 38% of tropospheric ozone along with ammonia, volatile organic compounds and particulate matter (Levine [1991;](#page-20-4) Bhattacharyya and Barman [2018;](#page-15-4)

Pollutant	Ethanol		<b>Biodiesel</b>		<b>Biogas</b>	Diesel
	22% ethanol blend	100% Ethanol	10% biodiesel	15% biodiesel		
Carbon monoxide	0.76	0.65	0.65	0.62	0.08	0.77
$NO_{x}$	0.45	0.34	0.83	0.89		0.79
Particulate matter	0.08	0.02	0.093	0.08	0.015	0.129
Unburned <b>Hydrocarbons</b>	0.004	0.02	0.22	0.16	0.35	0.37

<span id="page-5-0"></span>**Table 8.2** Emission pattern (g/km) of biofuel blends in automotive fuel

Compiled from Prasad et al. [\(2007\)](#page-22-5), Demirbas and Karslioglu [2007\)](#page-16-7)

Fagodiya et al. [2019;](#page-17-9) Kumari et al. [2018;](#page-19-10) Bali et al. [2021\)](#page-15-5). The 80% of total crop residue burned in 2017–18 in India was generated from straw of rice and wheat and sugarcane trash (Venkatramanan et al. [2021b\)](#page-24-5). The burning of residue from rice was reported highest from Punjab, Haryana and Western Uttar Pradesh (NPMCR [2014;](#page-21-5) Porichha et al. [2021\)](#page-22-6).

The energy consumption in India was 20.5 million tonnes in Dec, 2020 making it one of the largest importers of crude oil in the world (Trading.com. [2021\)](#page-24-6). The total energy demand is going to increase further over the years and is projected India will be in top three importing countries by 2025 (Kumar et al. [2020a;](#page-19-3) Lin and Raza [2020\)](#page-20-5). The use of alternative sources of transportation like biofuel reduce the emissions to the atmosphere and mitigate various environmental concerns (Bhuvaneshwari et al. [2019;](#page-15-6) Sahoo et al. [2020\)](#page-23-11). The power generation in India from biomass, bagasse and waste to energy accounts 1.6, 0.46 and 0.23% of total potential of renewable energy sources (MoSPI [2020\)](#page-21-9). The judicious management of the agro-wastes as potential feedstock for various biorefineries added value to it as resources (Sadh et al. [2018;](#page-23-2) Philippini et al. [2020\)](#page-22-3). The possibility of energy recovery from agro-wastes were studied by Vaish et al. [\(2016\)](#page-24-7) and Borja and Fernández-Rodríguez [\(2021\)](#page-15-7). Table [8.2](#page-5-0) compares the emission pattern of biofuel blends with diesel as automotive fuel. The emission reduction was observed from use of bioethanol, biodiesel and biogas as compared to diesel (Sharma et al. [2020a;](#page-23-1) Bušić et al. [2018;](#page-15-8) Turkcan [2020\)](#page-24-8).

The high value -added products from agro-residues are produced in cost effective way (Ibitoye et al. [2021;](#page-18-1) Kumar et al. [2020a;](#page-19-3) Bhatnagar et al. [2020\)](#page-15-3). These products found applications in pharmaceuticals, medical and cosmetic industries, chemical, food/feed, and pharmaceuticals (Philippini et al. [2020;](#page-22-3) Alexandri et al. [2021;](#page-14-0) Brandão et al. [2021\)](#page-15-9).

## **8.5 Conversion Technologies in Agro-Waste Biorefinery**

Biorefineries are alternative to petro-based refineries with the conversion of biomass to thermo-chemical energy and biobased products such as biopolymer and highvalue chemicals (Ubando et al. [2019;](#page-24-9) Ong and Wu [2020\)](#page-22-7). The conversion routes and technoeconomic feasibility of different biorefinery products mainly focused on biofuels and biochemicals from agro-wastes have been well discussed (Kumar et al. [2020;](#page-19-5) Kover et al. [2021;](#page-19-11) Ginni et al. [2021\)](#page-17-10).

The various biorefinery technologies for straw from rice, wheat and maize and agro- processing wastes such as rice husks, vegetable and fruit peels, sugarcane bagasse and oil cakes include fermentation, anaerobic digestion, pyrolysis, gasification and transesterification (Awasthi et al. [2020;](#page-14-1) Hiloidhari et al. [2020\)](#page-17-11). Further the products are recovered by stabilization, dewatering and refining (Liu et al. [2021;](#page-20-3) Kumar et al. [2018b;](#page-19-12) Paul and Dutta [2018\)](#page-22-8). The conversion of underutilized agro-wastes to clean biofuels (Fig. [8.4\)](#page-7-0) by thermal, chemical and biological routes help to meet energy demands and also the climate change mitigation (Prasad et al. [2020;](#page-22-0) Kumar et al. [2020a;](#page-19-3) Koytsoumpa et al. [2021\)](#page-19-13).

# *8.5.1 Bioethanol Biorefinery from Agro-wastes*

The global leaders in bioethanol production from agro-wastes are Asia, Europe, and North America (Najafi et al. [2009;](#page-21-10) Das et al. [2020\)](#page-16-8). The bioethanol production from second generation feedstock is more eco-friendly without compromising on food (Niphadkar et al. [2018\)](#page-21-0). The globally produced agro wastes had high estimated ethanol production potential which was sixteen times more than ethanol produced (Kim and Dale [2004\)](#page-19-2). Holmatov et al. [\(2021\)](#page-18-6) also estimated potential of residues produced from 123 crops in the world and its replacement power for fossil-based fuel. The ethanol blends with gasoline saves the fossil fuel consumption and improves the environmental quality (Ali et al. [2019;](#page-14-2) Barbosa et al. [2021\)](#page-15-10). The residue after the fermentation which are lignin rich able to produce electricity and steam (Mathew et al. [2018;](#page-20-6) Zhao et al. [2021\)](#page-25-0).

The pre-treatment is needed for lignocellulosic ethanol production in comparison to sugary feedstock (Jansen et al. [2017;](#page-18-7) Mathew et al. [2018\)](#page-20-6). The stages in ethanol production from agro-residues are pre-treatment, saccharification, fermentation of ethanol and finally the distillation (Carpio and de Souza [2017;](#page-15-11) Nogueira et al. [2020\)](#page-21-11). Bechara et al. [\(2018\)](#page-15-12) reviewed the sugarcane biorefinery for ethanol and electricity production.

The metabolism of hexoses undergoes phosphorylation and two moles of ethanol is produced (Eq. [8.1\)](#page-8-0) along with carbon dioxide in fermentation process (Ingram et al. [1998\)](#page-18-8). The three molecules of pentose generated (Eq. [8.2\)](#page-8-1) five molecules each of ethanol and  $CO<sub>2</sub>$  are produced by utilizing the carbohydrates from the agro-wastes by fermentation.



<span id="page-7-0"></span>Fig. 8.4 Sustainable biorefinery for agro-residues (Wyman 1990) **Fig. 8.4** Sustainable biorefinery for agro-residues (Wyman [1990\)](#page-24-10)

<span id="page-8-1"></span><span id="page-8-0"></span>
$$
C_6H_{12}O_6 \to 2C_2H_5OH + 2CO_2 \tag{8.1}
$$

$$
3C_5H_{10}O_5 \rightarrow 5 C_2H_5OH + 5CO_2 + energy (as ATP)
$$
 (8.2)

*Saccharomyces cerevisiae* widely ferment and convert C6 carbon sugars to ethanol (Zhang et al. [2016\)](#page-25-1). The yeasts such as *Pichia stipitis, Candida shehatae* and *Pachysolan tannophilus* are reported with ethanol producing capability from pentoses and hexoses (Rastogi and Shrivastava [2017;](#page-23-12) Ntaikou et al. [2018\)](#page-21-12). The immobilization of *Saccharomyces cerevisiae* and *Pichia stipitis* improved the ethanol production from rice straw pre-treated with microwave assisted ferric chloride by 1.27 times (Lü and Zhou [2015\)](#page-20-7). Watanabe et al. [\(2012\)](#page-24-11) confirmed ethanol production of 38 g/L from alkali pre-treated rice straw by *Saccharomyces cerevisiae* immobilized on photocrosslinkable resin beads. The ethanol production form sugarcane molasses by *S. cerevisiae* was 85–90% from batch fermentation and found increased to 94.5% in continuous fermentation (Sánchez and Cardona [2008\)](#page-23-13). The schematic representation of process integration (Kumar et al. [2020;](#page-19-5) Duque et al. [2021\)](#page-17-12) in bioethanol production from agro-wastes are given in Fig. [8.5.](#page-9-0)

#### *8.5.2 Biobutanol Biorefinery from Agro-Wastes*

The butanol based biorefinery from various agricultural residues was studied by Nanda et al. [\(2015\)](#page-21-2), Pereira et al. [\(2015\)](#page-22-9) and Pinto et al. [\(2021\)](#page-22-10).

Qureshi et al.  $(2007)$  reported the butanol production of 12 g/L from wheat straw hydrolysate by *Clostridium beijerinckii* P260. The potential of rice bran, fibres of maize, stover from maize, and bagasse from cassava for butanol production were already reported (Baral et al. [2018;](#page-15-13) Huang et al. [2019\)](#page-18-9). Molina-Guerrero et al. [\(2020\)](#page-21-7) estimated the sustainable butanol production potential of major residues of maize, wheat, barley and sorghum as well as waste generated from beans, coffee and sugarcane produced in Mexico. The electricity generation from these residues were also reported in high amounts.

Sanchez et al. [\(2017\)](#page-23-14) demonstrated biorefinery with value added products namely butanol, acetone, ethanol, hydrogen and biogas with the help of mixed culture by consolidated bioprocessing technology. The butanol biorefinery based on sweet sorghum bagasse following fed- batch fermentation was reported by Su et al. [\(2020\)](#page-24-12). Dutta et al. [\(2021\)](#page-17-13) demonstrated biobutanol biorefinery along with heat and power from the rice straw. The spent coffee grounds were used for producing butanol and also gallic acid and catechin (López-Linares et al. [2021\)](#page-20-8).

Many researchers studied the enhancement of ABE fermentation by immobilized cell technology (Gupta et al. [2020;](#page-17-14) Meramo-Hurtado et al. [2021\)](#page-21-13). The immobilization improved butanol or bioethanol tolerance with high viable cell densities, increasing fermentation rate and productivity (Jiang et al. [2009\)](#page-18-10).



<span id="page-9-0"></span>Fig. 8.5 Different steps in conversion processes for bio-alcohol production from agro-residues **Fig. 8.5** Different steps in conversion processes for bio-alcohol production from agro-residues

Qureshi et al.  $(2010)$  demonstrated the butanol production of 14.5 g/L from corn stover with*Clostridium beijerinckii* P260. The corn cob produced 12.3 g/L butanol by *C. saccharobutylicum* DSM 13864 (Dong et al. [2016\)](#page-16-9). The butanol production from wheat straw and barley straw by *C. beijerinckii* P260 was studied by Qureshi et al. [\(2007\)](#page-22-11) and Qureshi et al. [\(2014\)](#page-22-13) respectively. The *C. saccharoperbutylacetonicum* N1-4 able to produce 7.72 g/L butanol using rice bran (Al-Shorgani et al. [2012\)](#page-14-3). The alkali pre-treated rice straw improved butanol fermentation to 45.2 g, acetone and ethanol production of 17.7 g and 1.2 g respectively (Moradi et al. [2013\)](#page-21-14). The organosolv pre-treatment of rice straw for butanol production was reported by Amiri et al. [\(2014\)](#page-14-4) and Tsegaye et al. [\(2020\)](#page-24-13). Razi and Sasmal [\(2020\)](#page-23-15) had also used organic solvents as pre-treatment agent for butanol production form groundnut shells.

#### *8.5.3 Biogas from Crop Residues Biorefinery*

Various agro-wastes were studied by different researchers for anaerobic digestion and biogas production (Kumar et al. [2018a;](#page-19-7) Bušić et al. [2018\)](#page-15-8). The lack of direct competition with other conventional renewable feedstocks increased its importance as feedstock for biogas production.

The biogas production from wheat straw was studied by Somayaji and Khanna  $(1994)$  and Labatut et al.  $(2011)$ . Mancini et al.  $(2018)$  reported enhancement in biogas generation by chemical pre-treatments from wheat straw. The biogas production of 65 L/kg VS in 23 days (Isci and Demirer [2007\)](#page-18-11) and 149 L/kg in 30 days (Sahito et al. [2013\)](#page-23-16) from cotton stalk were reported. The cotton gin waste was studied for biogas production by Labatut et al. [\(2011\)](#page-20-9). The cotton stalk was also studied for methane production by Zhang et al. [\(2018\)](#page-25-2).

Liew et al. [\(2012\)](#page-20-11) demonstrated biogas production of  $81.2 L kg^{-1}$  and  $66.9 L kg^{-1}$ from corn stover and wheat straw respectively. The whole stillage (85%) codigested with cattle manure (15%) produced biogas of 0.31 L CH<sub>4</sub> g<sup>-1</sup> VS<sub>added</sub> (Westerholm et al. [2012\)](#page-24-15) in 45 days. The co-digestion of goat manure with corn stalks, rice straw and wheat straw enhanced biogas production (Zhang et al. [2013\)](#page-25-3). The methane production by co-digestion of wastes from banana, canola, cotton, rice, sugarcane and wheat with buffalo dung was also demonstrated by Sahito et al. [\(2013\)](#page-23-16). The residues of maize, sorghum and bedding straw from cattle farm were studied for biogas production and found methane yields of 267 L CH<sub>4</sub> kg<sup>-1</sup> VS (Kalamaras and Kotsopoulos [2014\)](#page-18-12). Afif et al. [\(2020\)](#page-14-5) demonstrated the improved biogas generation from cotton stalks pre-treated with supercritical carbon dioxide.

The other agro-wastes used for methane production by anaerobic fermentation were food and vegetable wastes, oat straw, olive husk and maize stalks (Paul and Dutta [2018;](#page-22-8) Nwokolo et al. [2020\)](#page-21-15).

# *8.5.4 Biohydrogen Biorefinery from Agro-Wastes*

The biohydrogen is a renewable, alternative fuel combined with electricity production from fuel cell technology makes it a cleanest and efficient fuel source (Bundhoo [2019\)](#page-15-14). The biochemical route of biohydrogen production from agro-residues was by bio-photolysis and anaerobic fermentative processes, either dark or photo fermentation (Bušić et al.  $2018$ ; Anwar et al.  $2019$ ). The major microbes associated with biohydrogen production are micro algae, cyanobacteria, photosynthetic and fermentative bacteria (Goswami et al. [2021;](#page-17-15) Rather and Srivastav [2021\)](#page-23-17). The biohydrogen yield from acetate and butyrate fermentation was 4 mol and 2 mol of hydrogen respectively per molecule of glucose (Vijayaraghavan and Soom [2006\)](#page-24-16). Kannah et al. [\(2018\)](#page-19-14) demonstrated the efficient biohydrogen production from rice straw by combinative dispersion thermochemical disintegration. Lopez-Hidalgo et al. [\(2017\)](#page-20-12) demonstrated the biohydrogen production from mixture of cheese whey and wheat straw hydrolysate. Mohanto et al. [\(2020\)](#page-20-13) reported the fruit waste can be used for hydrogen production by *Clostridium* strain BOH3. Tinpranee et al. [\(2018\)](#page-24-17) screened blue green algae collected from coastal waters of Thailand for the production of hydrogen.

# *8.5.5 Biodiesel Biorefinery from Agro-Wastes*

The agro-residues with lipid content mainly oilseed crops are suitable feedstock for biodiesel production. The biodiesel is commonly produced by transesterification in the presence of a catalyst and alkali with production of mono-alkyl esters (Bušić et al. [2018;](#page-15-8) Demirbas and Karslioglu [2007\)](#page-16-7). The stearic acid, oleic acid, linoleic acid and linolenic acid are common fatty acids found in oilseeds with 18 carbon atoms and no, mono, di and tri- unsaturated bonds respectively, and a few oilseeds also have palmitic acid (16:0), lauric acid (12:0) type of fatty acids. The chemical reaction representing the trans-esterification for biodiesel production is shown in Fig. [8.6](#page-11-0) as follows:



<span id="page-11-0"></span>**Fig. 8.6** Biodiesel production by transesterification of agro-wastes with oil content (Bušić et al. [2018;](#page-15-8) Demirbas et al. [2016\)](#page-16-10)

The  $R_1$ ,  $R_2$  and  $R_3$ ' presented in the reaction are carbon chains of fatty acid and 'R' is the alkyl group of alcohol used in transesterification.

The oilcake produced after oil expulsion also contains oil and can be a suitable raw material for biodiesel production (Jain and Naik [2018;](#page-18-13) Budžaki et al. [2019\)](#page-15-15). The rice bran, a by-product of rice mill had oil content with biodiesel production potential (Mazaheri et al. [2018;](#page-20-14) Hoang et al. [2021\)](#page-18-14). Quayson et al. [\(2020\)](#page-22-14) demonstrated the palm kernel shells and palm oil mill effluent to biodiesel with immobilized lipase from recombinant *Fusarium heterosporum*. Khounani et al. [\(2021\)](#page-19-15) produced bioethanol, biodiesel, biogas and other bioproducts from safflower biorefinery.

# *8.5.6 Syngas and Fischer–Tropsch Derivatives from Agro-Waste Biorefinery*

The gasification for syngas production from agro-wastes is a thermo-chemical conversion technology and it contains carbon monoxide, hydrogen and other hydrocarbons. The syngas has its direct application in internal combustion engines and for combined heat and power generation. The syngas had been converted to liquid fuel such as methanol, dimethyl ether and hydrogen and hydro-cabons produced by the Fischer–Tropsch process (Cerone and Zimbardi [2018;](#page-16-11) Dieterich et al. [2020\)](#page-16-12). Fischer–Tropsch process is a polymerization process with catalyst (iron, cobalt or ruthenium) with high temperature Fischer–Tropsch Synthesis (FTS) resulting in short-chain hydrocarbons and light olefins and waxes and long-chain hydrocarbons from low temperature FTS (Yahyazadeh et al. [2021\)](#page-24-18). The gaseous fuels produced from agro-residues are more economical and sustainable (Mallikarjuna et al. [2021\)](#page-20-15).

# *8.5.7 Value-Added Chemicals from Agro-Wastes*

The biorefinery based on biofuels and biochemicals from agro-residues are well studied by various researchers (Bilal et al. [2017;](#page-15-16) Bhatnagar et al. [2020\)](#page-15-3). The organic acids are an important group of bio-chemicals produced from agro-wastes (Porro and Branduardi [2017;](#page-22-15) Sheldon [2018\)](#page-23-18). The major organic acids generated by fermentation of lignocellulosics were succinic acid, adipic acids, glutamic acid, aspartic acids, itaconic acid and 3-hydroxypropionic acids (Corato et al. [2018;](#page-16-13) Misra et al. [2021\)](#page-21-16). The value-added chemicals like sorbitol, p-xylene, hydroxymethyl furfural, furans, levulinic acids were derived from glucose units of cellulosic materials (Pattnaik et al. [2021\)](#page-22-16). The glycerol is produced as a byproduct in transesterification of oil containing agro-residues (Chilakamarry et al. [2021\)](#page-16-14). The biochemicals which can be produced as derivatives of glycerol are propylene glycol, 1,3 propane-di-ol, acrolein

and epichlorohydrin (Lima et al. [2021\)](#page-20-16). The lignin derivatives such as syngas, hydrocarbons, phenols, vanillin, vanillic acids and carbon fibre fillers, composites, adhesives, etc. are also value-added products from agro-wastes (Adhikari et al. [2018;](#page-14-7) Bhatnagar et al. [2020\)](#page-15-3).

#### **8.6 Challenges in Agro-Waste Based Biorefinery**

The economic viability is major limitation of biomass based biorefinery (Paul and Dutta [2018;](#page-22-8) Hassan et al. [2019;](#page-17-4) Raud et al. [2019;](#page-23-6) Bhatnagar et al. [2020;](#page-15-3) Kumar et al. [2020a\)](#page-19-3). The major challenges are

- High capital cost and operational costs
- Biomass supply chain
- Less-developed conversion techniques
- Problems associated with scale up processes
- Constraints involved in down-stream processing.

One another bottleneck in viability of agro-waste based biorefineries is the pretreatment for fermentation processes (Philippini et al. [2020\)](#page-22-3). The pre-treatment of agro-wastes is essential to reduce recalcitrance of lignocellulosics for enzymatic hydrolysis (Baral et al. [2018;](#page-15-13) Mancini et al. [2018;](#page-20-10) Mahmood et al. [2019\)](#page-20-17). The technical hurdles in transportation of agro-wastes to the biorefinery, processing and product recovery were assessed by Chandel et al. [\(2018\)](#page-16-15) and Kumar et al. [\(2020a\)](#page-19-3).

The cellulosic ethanol has been commercialized by multi-national companies like Raizen (Piracicaba, Brazil), Gran-bio (S. João dos Milagres, Brazil) and POET-DSM (Emmetsburg, USA). The POET-DSM has also been marketing bio-based succinic acid. The chemicals from cellulosic materials are also produced and commercialized by Dow-DuPont (1,3-Propanediol, 1,4-Butanediol), Clariant-Global bioenergies-INEOS (bio-isobutene), Braskem (Ethylene, polypropylene). The torrefaction, steam explosion and hydrothermal carbonization improved the fuel efficiency of pellets from agro-residues. The advanced techniques like solid-liquid extraction (SLE), and pulsed electric fields (PEF) and membrane and resin techniques were applied for extraction and production of bioactive compounds from agro residues (Nguyen [2017\)](#page-21-0).

The National Policy on biofuels [\(2018\)](#page-21-17) aimed at a target of achieving 20% of biofuels in our country by 2030. The policy focussed on agro-residues to reach the target mainly by use of damaged food grains of rice and wheat unsuitable for human consumption to be diverted to fermentation process for producing ethanol. This will meet the requirement of ethanol in blending with gasoline and helps in mitigating environmental pollution as well as attaining energy security.

The biorefineries are seemed to be more sustainable for biochemical production than the biofuels.

# **8.7 Conclusion**

The agro-residues from the crop harvesting and processing mainly composed of cellulose, hemicellulose and lignin polymers. These compounds by means of thermochemical and biochemical conversion routes are able to convert to biofuels and biochemicals. The fermentation technology is the highly recommended technique involved in the production of bioethanol, biobutanol, biohydrogen and biogas. The gasification process had syngas as products that can further transformed to biochemicals. The oil containing agro wastes are good source for biodiesel and glycerol production. The biorefineries based on agro residues are second generation biorefineries and reduce the negative impacts on environment and help to move towards sustainable development. The advanced and effective technologies with an integrated and zero-waste approach overcome the technical and economic challenges presently faced by the agro-waste based biorefineries and enable towards commercialization.

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