

Chemicals and Fuels Production from Agro Residues: A Biorefinery Approach



Desikan Ramesh, Iniya Kumar Muniraj, Kiruthika Thangavelu
and Subburamu Karthikeyan

Abstract Alternative fuel production technology in order to combat the present scenario of climate change issues has been in the transition stage of generating high-value low volume chemicals, fuels and low-value high volume bulk products (biofuels). This concept of biorefinery is the future of biomass processing technologies where complete utilization of biomass and zero release of waste can be achieved. The agro residue biorefinery aims in sustainable approach which provides a good solution for sustainable ways of utilizing agricultural residues. Agro residues are by-products of agricultural crop production and processing, which are abundantly available at lower price. Agro residues are one of the major resources of unexploited potential lignocellulosic feedstocks. It includes straws, leaves and plant materials left in the field after harvesting of the crop. Its characteristics would vary with crops, species and environmental conditions. Annual agro residue production potential in India is ca. 550 MT. Currently, most of the residues are underutilized or burnt in situ, creating serious environmental pollutions. In order to utilize and effective disposal of these wastes, several methods are tried for tapping the energy/bioproductions from various crop residues via biochemical or thermochemical conversion routes. Biorefinery technologies can offer a platform for production of high-value chemicals and fuels from these residues, which are value-added products as well as provide more income for agriculturists. This chapter aims in bringing out sources of agro residues, the current state of the art of biomass processing and conversion viable technologies, and recent developments in the biorefinery of agro residues, and finally sheds light on commercialization of agro residue biorefinery.

D. Ramesh (✉)

Horticultural College & Research Institute for Women, Tamil Nadu Agricultural University,
Tiruchirappalli, India
e-mail: rameshd@tnau.ac.in

I. K. Muniraj

Kumaraguru Institute of Agriculture, Sakthinagar, Erode, India

K. Thangavelu · S. Karthikeyan

Agricultural Engineering College and Research Institute, Tamil Nadu Agricultural University,
Coimbatore, India

Keywords Biorefinery · Biochemicals · Thermochemical conversion technologies · Paddy straw

1 Introduction

Petroleum products play a major role in our modern life, and its continued usage has created negative impacts on the environment. Fossil fuels-based transport sector is the best example of negative impacts on the environment such as air pollution, climate change and global warming, and also affects nation's energy security and economy. Apart from this, emissions from the in situ burning of biomass stubble are the other causes to increase the CO₂ level and also air/land pollution. According to the World Energy Outlook 2002 (IEA 2002), the per capita emissions of OECD and transition economies are projected to reach 13 tonnes and 11 tonnes, respectively, in 2030. Renewable energy sources are mainly focused on alternatives to fossil fuels and their associated products due to its renewability, plenty available and also low cost. Population growth and unequal social development have exacerbated the vulnerability of our societies to the fragility of the world's climate system and the impacts of natural events. At this juncture, attention is naturally focused on biomass as energy resource looking for alternate energy sources, which can make a significant contribution to satisfy the energy needs of society with environmental friendly (Tao et al. 2013). Among the different biomass resources, lignocellulosic biomass feedstocks are potential candidates for promoting the transition from the petroleum-based economy to bioeconomy of the country for a sustainable development, and it reduces the depends on foreign oil imports and money (Raman et al. 2015; Xu et al. 2016). Agro residues are the main resource that falls under lignocellulosic biomass feedstocks category. It was obtained as by-products from agricultural crop production and processing operations. It includes straws, leaves and plant materials left in the field after harvesting of the crop. Its characteristics would vary with crops, species and environmental conditions (De Bhowmick et al. 2018). This residues are one of the unexploited potential resources, which offer a new business platform for production of variety of biofuels, fine chemicals and value-added products to displacing petroleum-based products. An estimation shows that theoretical energy potential of global agricultural residues produced in a year is ranged from 14.6 to 123 EJ (WBA Global Bioenergy Statistics 2017). Effective utilization of these residues is currently a big challenge for industries involved in production of biofuels and biochemical/bioproductions. Bioethanol production from this feedstock consumes more energy and processing cost than that of first-generation biofuel crops. Production of multiple products from agro residues is a viable solution to minimize the biofuel's price to compete with conventional fuels and also minimize the waste generation in each bioprocessing of biofuel production. Similar to a petroleum refinery, the multiple products from these wastes can be achieved via selected processes of different biomass conversion technologies.

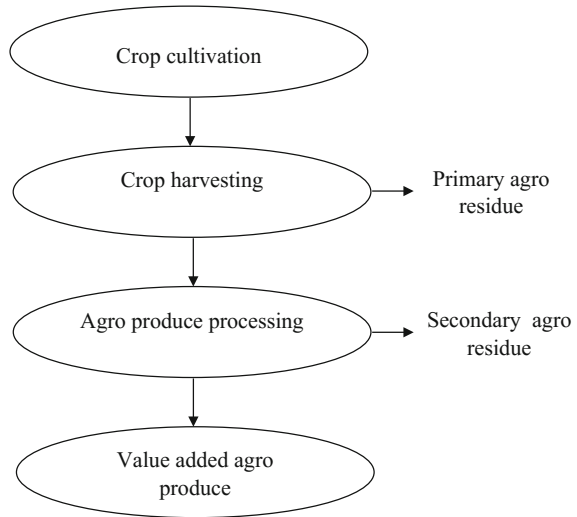
Biorefinery mainly focused on bioenergy as primary product and chemicals as secondary products from biomass resources and vice versa. The biorefinery is a good option for effective utilization of renewable feedstocks for multiple products generation (bioenergy, biofuel and fine biochemicals) and minimizes the huge quantity of waste (Ahring and Westermann 2007; Cabeza et al. 2016; Christopher et al. 2017; Dominguez et al. 2014). This will help in safe handling and disposal of bulk quantity of wastes and lower the pollution in the environment. In other words, the by-products of the first process would be used as substrate/raw materials for next product production. For example, the biorefinery approach is applied to sugarcane crop to obtain bioethanol and fine chemicals. So far, four generations are developed for biorefineries, viz. first-generation (food crops or animal fat), second-generation (nonfood crops), third-generation (mix of different biomass feedstocks) and fourth-generation (vegetable oil). Among them, first-generation biorefineries are commercialized in different countries. Biorefinery offers energy and value-added products as well as provide more income to agriculturists (Zhang et al. 2016).

In this chapter, the different types of agro residues and their sources, viable conversion technologies, biorefinery approaches, constraints in commercialization of biorefineries, and paddy straw as a potential source for biorefinery are briefly discussed.

2 Agro Residues and Resources

Agro residues are obtained after harvesting or processing or both operations of agricultural crops. It may be in the form of solid or semi-solid, and it depends upon the agro products obtained. Generally, the agro residues can be classified into primary and secondary residues (Fig. 1). In case of primary residues, the residues are collected in the field itself after the harvesting of main agro product from crop, e.g. plant materials, stalks, leaves, etc. The secondary residues are generated from during the processing of main agricultural produce, e.g. rice husk, maize cob, etc. Residue-to-product ratio (RPR) is an important terminology related to residue calculation for a particular crop, and the value of RPR varies from crop to crop. RPR is defined as the ratio between the weight of the crop residue to the total weight of agro product yield for the selected crop. The range values of RPR for primary and secondary agro residues of different agricultural crops are 0.05–4.00 and 0.15–2.00, respectively (Table 1). RPR value is more useful to predict the quantity of agro residue generated for the selected crop. Multiplication of crop yield with RPR value would give waste generation for the calculated crop and RPR value also used in biomass assessment studies conducted for a location/state/country. Theoretical estimation of agro residues production per year for India and world is 500–550 MT and 3.6–17.2 billion tonnes (IARI 2012; WBA Global Bioenergy Statistics 2017). A huge amount of these wastes should be used effectively for multiple products productions via suitable biorefinery approach.

Fig. 1 Illustration of primary and secondary agro residue generated in harvesting and processing of agricultural crops



2.1 Availability of Agro Residues

During the processing of agricultural crops such as paddy, wheat, sugarcane and maize, a copious amount of residues are generated, for instance, 1 tonne of sugarcane generates 300 kg of bagasse, 1 tonne of paddy generates 0.75 tonnes of straw and the equal amount of stover is generated while processing corn. All these residues are rich in sugars and can be utilized for the biorefinery. A significant quantity of the residues will be used for fodder, manure and local use for trashing house. Globally, various countries generate agricultural residues in enormous amounts, and their availability is depicted in Fig. 2. India achieved self-sustainability in food grain production, and agriculture is main resource income for the farming community in most of the rural villages. Eight crops, viz. rice, wheat, bajra, jowar, sugarcane, cotton, groundnut and oilseeds, are majorly cultivated in 11 different states of India. The details of annual crop residues generated, surplus availability and their power generation potential are presented in Table 2. An estimate shows that annual power potential from agro residues alone for India is calculated as 18729.9 MWe from 511 MT of wastes.

Uttar Pradesh and Punjab are leading states in major agro residues production from both wheat and paddy crops. Annual agro residue production, major crops and types of residues in India are presented in Table 3. Among the crops, sugarcane, rice and wheat crops generate major share for agro residues generation in India. Sugarcane crop production and processing can contribute an amount of 2,76,250 metric tonnes of primary and secondary residues and paddy stands as a second largest contributor in our country.

Table 1 The RPR ratio for different agricultural crops

Crop group	Crop	Residue		RPR	References
Cereals	Rice	Primary	Straw	1.50	Hiloidhari and Baruah (2011a, b)
		Secondary	Husk	0.20	Singh et al. (2008a, b, c)
	Wheat	Primary	Stalk	1.50	Hiloidhari et al. (2014) Raveendran et al. (1995) Friedl et al. (2005)
		Secondary	Pod	0.30	
	Maize	Primary	Stalk	2.00	
		Secondary	Cob	0.30	
	Bajra	Primary	Stalk	2.00	
		Secondary	Cob	0.33	
			Husk	0.30	
	Barley	Primary	Straw	1.30	
	Jowar	Primary	Stalk	1.70	
		Secondary	Cob	0.50	
Husk			0.20		
Millets	Small millet	Primary	Straw	1.20	
	Ragi		Straw	1.30	
	Kodo millet		Stalk	1.16	
Oilseeds	Mustard and rapeseed	Primary	Stalk	1.80	
	Sesame		Stalk	1.20	
	Linseed		Stalk	1.47	
	Niger		Stalk	1.00	
	Safflower		Stalk	3.00	
	Soybean		Stalk	1.70	
	Groundnut		Stalk	2.00	
			Secondary	Shell	0.30
Sunflower	Primary	Stalk	3.00		
Pulses and legumes	Tur(arhar)	Primary	Stalk	2.50	
		Secondary	Husk	0.30	
	Avare	Primary	Stalk	1.10	
	Lentil	Primary	Stalk	1.80	
	Guar		Stalk	2.00	
	Green gram		Stalk	1.10	

(continued)

Table 1 (continued)

Crop group	Crop	Residue		RPR	References
		Secondary	Husk	0.15	Biomass Knowledge Portal
	Horse gram	Primary	Stalk	1.30	
	Red gram		Stalk	1.10	
	Moth bean		Stalk	1.80	
	Peas and beans		Stalk	0.50	
Sugar crop	Sugarcane	Primary	Top and leaves	0.05	Singh et al. (2008a, b, c)
		Secondary	Bagasse	0.33	
Horticulture	Banana	Secondary	Peel	3.00	Wilaipon (2009)
	Coconut	Primary	FronD	4.00	Rahman (2006)
		Secondary	Husk and pith	0.53	Minowa et al. (1998)
			Shell	0.22	Biomass Knowledge Portal
	Areca nut	Primary	FronD	3.00	Hiloidhari et al. (2014)
Secondary		Husk	0.80	Pilon (2007)	
Fibres	Cotton	Primary	Stalk	3.80	Jekayinfa and Scholz (2009)
		Secondary	Husk	1.10	Hiloidhari et al. (2014)
			Boll shell	1.10	Caglar and Demirbas (2001)
	Jute	Primary	Stalk	2.00	Asadullah et al. (2008)
Spices and condiments	Cardamom	Primary	Stalk	0.64	Biomass Knowledge Portal
	Coriander		Stalk	1.15	
	Cumin seed		Stalk	1.55	
	Dry chilly		Stalk	1.50	
	Turmeric		Stalk	0.30	
Plantains	Coffee	Primary	Pruning and Wastes	4.00	
		Secondary	Husk	0.50	
	Tea	Primary	Sticks	1.00	
	Rubber	Primary	Wood	3.00	
		Secondary	Wood	2.00	
	Tobacco	Primary	Stalk	1.00	
Vegetables	Onion	Primary	Stalk	0.05	

(continued)

Table 1 (continued)

Crop group	Crop	Residue	RPR	References
	Dry ginger		Stalk	0.05
	Garlic		Sheath	0.25
			Stalk	0.05
Tubers	Potato	Primary	Leaves	0.76
			Stalk	0.05
	Sweet potato		Stalk	0.10
	Tapioca		Stalk	0.75
Medicinal	Isabgol	Primary	Stalk	1.10

Source production data were taken from <http://faostat3.fao.org/browse/Q/QC/E> and residues values were obtained manual conversion ratio from each crop yield

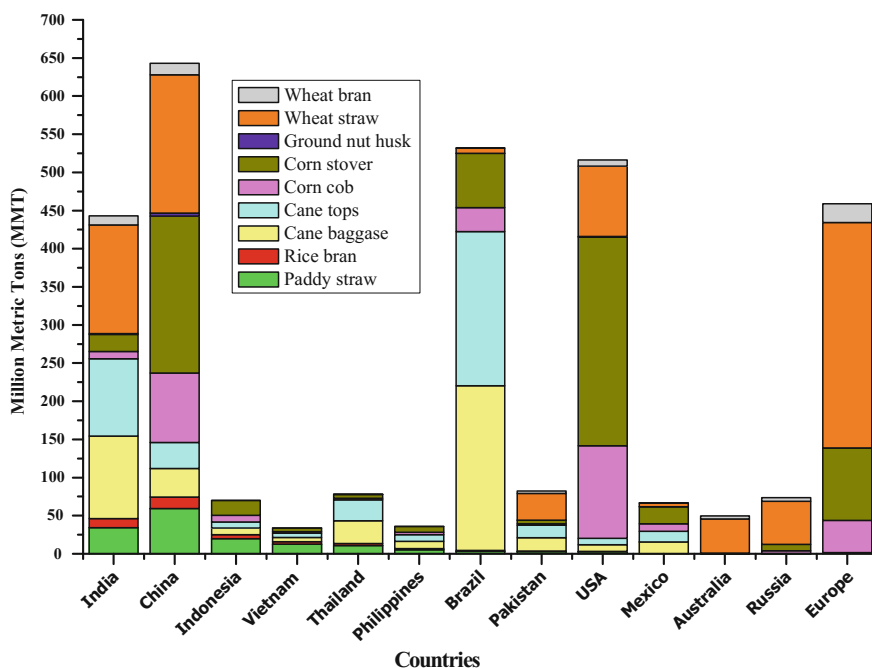


Fig. 2 Total agricultural residues generated by various countries in 2012

Table 2 Estimated annual agro residues production, surplus availability and their power production potential in India

State	Agro residue production (kT/yr)	Surplus (kT/yr)	Power potential (MWe)
Uttar Pradesh	60322.2	13753.7	1748.3
Punjab	50847.6	24843.0	3172.1
Maharashtra	47624.8	14789.9	1983.7
West Bengal	35989.9	4301.5	529.2
Karnataka	34167.3	9027.3	1195.9
Madhya Pradesh	33344.8	10329.2	1373.3
Rajasthan	29851.3	8645.6	1126.7
Haryana	29034.7	11343.0	1456.9
Gujarat	29001.0	9058.3	1224.8
Bihar	25756.9	5147.2	640.9
Andhra Pradesh	24871.7	4259.4	520.8
Tamil Nadu	22507.6	8899.9	1159.8
Odisha	20069.5	3676.7	429.1
Telangana	19021.5	2697.2	342.5
Kerala	11644.3	6351.9	864.4
Assam	11443.6	2436.7	283.7
Chhattisgarh	11272.8	2127.9	248.3
Jharkhand	3644.9	890.0	106.7
Uttarakhand	2903.2	638.4	81.0
Himachal Pradesh	2896.9	1034.7	132.6
Jammu and Kashmir	1591.3	279.5	37.1
Manipur	909.4	114.4	14.3
Goa	668.5	161.4	20.9
Mizoram	511.1	8.5	1.1
Nagaland	492.2	85.2	10.0
Arunachal Pradesh	400.4	74.5	9.2
Sikkim	149.5	17.8	2.3
Meghalaya	61.1	91.6	11.3
Tripura	40.9	21.3	3.0
Total	511040.9	145105.7	18729.9

Source <http://biomasspower.gov.in/> (as per May 20, 2016)

Table 3 Details of annual residues production from main crops in India (Thomas et al. 2017)

Crop	Annual production, metric tonnes	Types of agro residues generated
Sugarcane	2,76,250	Bagasse, top and leaves
Rice	1,45,050	Stalks, straw
Wheat	78,000	Pods, stalks
Banana	80,000	Residue, cobs
Maize	18,000	Stalks, fronds
Coconut	13,125	Husk and pith, shell
Millets	12,410	Stalks, cobs
Bajra	7690	Stalks, husks
Cassava	6060	Solid waste, starch from roots
Arhar	1950	Husks, stalks

3 Biorefinery

Biorefinery involves several sequences of operations to disintegrate/convert the biomass into different bioproducts (biochemicals/biofuels/biomaterials) and bioenergy, in other words, conversion of biomass into useful bioproducts via efficient biomass conversion technologies with minimal waste generation. The biomass conversion technologies may be based on thermochemical, chemical or biochemical conversion routes and/or their combinations. The biorefinery is a facility that integrates biomass conversion process and equipment to produce fuels, power and chemicals from biomass (NREL 2009). In the biorefinery, transformation of recovered sugars from agro residues into fuels and chemicals are achieved by combination of new fermentation and thermochemical processes. Biorefinery is a clear example of industrial symbiosis, as it involves careful management and utilization of materials, products and wastes in a desirable way. There are three phases of biorefinery known, viz., phases I, II and III (Octave and Thomas 2009).

3.1 Phase I Biorefinery

The phase I biorefinery utilizes grain as feedstocks such as corn and wheat. The main difference in phase I and phase II biorefinery is that it has fixed processing capabilities and produces a fixed amount of ethanol and other feed products.

3.2 Phase II Biorefinery

It has more flexibility than phase I, wherein it can produce more end products and far more flexibilities. Examples of corn dry milling and wet milling are phase I and phase II biorefinery, respectively. Under phase II biorefinery if corn is used as feedstock, it can produce multiple products such as gluten feed, high fructose and corn syrup besides starch, glucose and dextrose, ethanol, gluten meal and corn oil.

3.3 Phase III Biorefinery

Recently, phase III biorefinery gains attention; it combines a mix of biomass feedstocks and yields an array of products by employing the combination of different technologies. Although it is in the developing stage, phase III system offers more advantages than other phases. It can simultaneously operate wet and dry biomasses both treated and untreated, recovered sugars such as cellulose, hemicellulose would be combined or processed in batch wise and high-value chemicals would be generated. Lignin would be used in direct combustion to generate steam and electricity.

3.4 Types of Biorefinery

The general scheme on biorefinery initially starts with separation of plant components by grinding followed by a fractionation by biological and physicochemical technologies. This enables the role of biomass extracts to be used as functional compounds. The next step is synthesis of agro-industrial products and development of a large number of bio-based products. Classification of biorefineries based on different types of feedstock used is shown in Fig. 3.

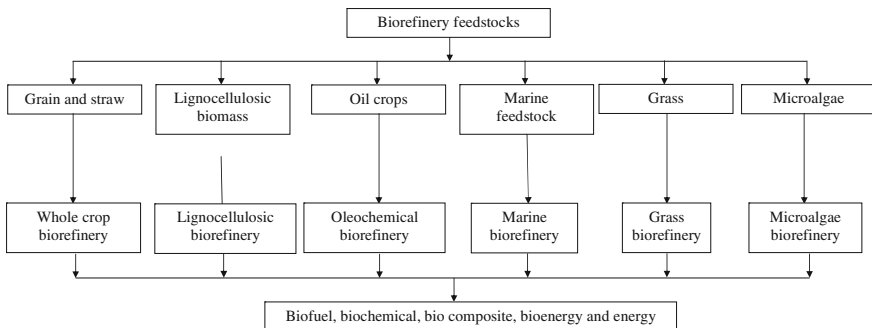


Fig. 3 Biorefinery technologies used for different feedstocks

4 Important Energy and Chemicals Recovery Routes Under Biorefinery Approach for Agro Residues

Biomass energy conversion technologies are mainly divided into three categories, viz. thermochemical, biochemical and chemical conversion technologies to obtain different types of biofuels, bioenergy and fine chemicals from biomass feedstock. Among the four different biofuel generation technologies, first-generation biofuel is successfully commercialized in different countries. Other biofuel generation technologies are still in infancy stage to address the challenges involved in optimizing process conditions and also reduce the processing cost. The additional amount spent on 2, 3 and 4G technologies for biofuel production should have an impact on fuel price and difficult to compete with conventional fossil fuels.

4.1 Anaerobic Digestion

A microbial consortium is involved in biodegradation of organic matter in four different consecutive steps under anaerobic conditions to yield methane-rich gas. Anaerobic digestion is also called as biomethanation process. Two end products obtained from anaerobic digestion process are gaseous biofuel and biodigested slurry. The gaseous fuel is referred as biogas, and it can be used for thermal applications, lighting and engine running. Most of the agro residues are suitable to produce biogas via anaerobic digestion process (Adney et al. 1991).

4.2 Gasification

It is one of the thermochemical conversion technologies used to convert the biomass feedstock into gaseous biofuel. Gasification involves thermal cracking and incomplete combustion of biomass under a limited amount of air/O₂ supply. Gaseous fuel generated at the end of the gasification process. Depending on the oxidizing agents used in gasification, gaseous fuel is referred as producer gas for air supply and syngas for O₂ supplied. The gas compositions of the producer gas are % carbon monoxide, % hydrogen and traces of methane. The biomass gasifier is a device used for this purpose. Based on the flow of oxidizing agent and feedstock materials, the biomass gasifier is mainly classified into three categories, viz. downdraft, updraft and cross draft gasifier. For gasifying of biomass with higher moisture content, supercritical water or plasma gasification can be used. Deterrents of wet biomass gasification are the higher investment, more energy and inputs required and the skilled technical person required to operate this equipment (Chen et al. 2015).

4.3 Pyrolysis

Thermal degradation of biomass feedstocks occurred in between 350 and 500 °C under the absence of air or O₂. The end products of this process may be in the form of gaseous fuel or solid fuel or liquid biofuel. The choice of end product mainly depended on the reaction temperature, heating rate, particle size and reaction time (Chen et al. 2017).

4.4 Combustion

Combustion is the process of burning biomass feedstocks under excessive aerated environment to generate the heat energy. Several factors that have an influence on heat release during combustion process are biomass composition, biomass types and plant age. Generally, combustion is used in the last stage of biorefinery approaches for converting entire biomass into heat energy for electricity production and ashes. In situ burning of agricultural residues is not a new technique, and farmers adopting this technique for quick and easy disposal of agro residues for land preparation for next crop cultivation in the consecutive season (Byun and Han 2016; Eynde et al. 2016; Hellier et al. 2015).

4.5 Biochemicals

Effective utilization of agro residues would lead to additional income, low waste generation and reduced dependence on other conventional resources (Beller et al. 2015). The biochemicals can be derived from different components of residues such as cellulose, hemicellulose and lignin. Sugars in the form of polysaccharide both structural and storage are the important part of the plant. However, in general, the sugars are always in close association with lignin. The biorefinery would first separate the sugar component of the plant without much damage and further remove the other components. Among the sugars, simple sugars like glucose and hexoses are the predominant compounds for many applications like ethanol for biofuels. The derived product from glucose is a lactic acid, which serves as a basic molecule in chemistry (Bouaid et al. 2010). For example, lactate esters are used as green solvents in industries. Further transformation of lactic acid into high-value chemicals such as acrylic acid and 1,2 propane diol would also be possible. Succinic acid is one of the important derivatives of glucose that can also be produced by chemical inducers.

5 Selection of Biorefinery Technologies

Biochemical composition of agro residues would vary from crop to crop, genotypes, season to season, soil and environmental conditions. Several types of biomass conversion technologies are employed in the biorefinery approaches. The selection of appropriate technologies is strongly based on feedstock composition and the focused end products. The biochemical composition of different agro residues is presented in Table 4. Three major components of this kind of biomass are varied for different resources, and values of cellulose, hemicellulose and lignin are in the range of 10–53%, 0.15–65% and 5–45%, respectively. For example, an agro residue with higher carbohydrate content is suitable for biochemical conversion route to produce bioalcohols from fermentable sugars, whereas biomass composition is not a major issue for thermochemical conversion route (Henry 2018). And also, the biomass with higher moisture (more than 50%) would not be suitable for most of the thermochemical conversion methods such as gasification and combustion process. Selection criteria are based on raw materials, end products, technologies used, processing cost and the market value of end products. If energy production is focussed, combustion is the best route among the thermochemical conversion technologies. Benefits of combustion technologies are less operational costs and higher energy output than other technologies. A rough estimate showed that production of biochemical, biofuels and energy generation from biomass may utilize 20, 40, and 40% of biomass used for the process (de Jong and Jungmeier 2015). The biorefinery technology is classified based on the number of feedstocks used, process involved and end products produced.

6 Constraints in Commercialization

The sustainability of biorefinery industries is depending on efficient conversion technologies, government policies, incentives and also techno-economical viable process availability. Even though each technology has its own merits and demerits, there are several biomass power plants in India shut down their operations. The reason is non-availability of feedstock, higher feedstocks price and fewer incentives. In order to avoid this kind of situation for agro residue-based biorefineries, the following points should be considered before the biorefinery plant installation:

- (a) Survey on crop residue assessment,
- (b) Feedstock collection via contract farming,
- (c) Policy for promoting biorefinery and
- (d) Good supply chain and logistics.

Table 4 Biochemical composition of different agro residues

Agro residues	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Rice straw	28.1–43.77	20.47–31.42	4.84–23.3	Chen et al. (2011a, b), ECN—Phyllis2, Prasad et al. (2007a, b), Rai et al. (1989), Samklong et al. (2010)
Wheat straw	28.8–51.5	10.5–43	5.4–30	ECN—Phyllis2, Gao et al. (2016), Mani et al. (2006a, b), Esteghlalian et al. (1997), Motte et al. (2014)
Almond shell	29.0–31.1	28.0–38.0	27.7–35	Dhyani and Bhaskar (2017)
Barley straw	31–45	21.9–38	6.3–19	Saini et al. (2015), Mani et al. (2006a, b), Nigam et al. (2009), Cai et al. (2017)
Cashew nut shell	41.3	18.6	40.1	Dhyani and Bhaskar (2017)
Coir pith	36–43	0.15–0.25	41–45	Saini et al. (2015)
Corn straw	27.9–42.6	14.8–21.3	8.2–19	Diaz et al. (2015), Bilal et al. (2017a, b)
Eucalyptus	45–51	11–18	29	Bilal et al. (2017a, b)
Flax straw	36.7	34.4	28.9	Dhyani and Bhaskar (2017)
Groundnut shell	35.7	18.7	30.2	Dhyani and Bhaskar (2017)
Horticultural waste	34.5	28.6	36	Bilal et al. (2017a, b)
Jute fibres	45–53	18–21	21–26	Bilal et al. (2017a, b)
Millet husk	33.3	26.9	14	Dhyani and Bhaskar (2017)
Nut shells	25–30	25–30	30–40	Bilal et al. (2017a, b)
Oat straw	31–39.4	27–38	16–19	Nigam et al. (2009), Sanchez (2009)
Palm fibre	35.4	19.9	27.3	Laghari et al. (2016)
Rice husk	25–44.12	12.0–29.3	7.28–31	Nordin et al. (2007), Ludueña et al. (2011), Wang et al. (2012), Braga et al. (2013), Cai et al. (2017)
Rice straw	28–37.81	22.3–28	12–19	Prasad et al. (2007a, b), Chen et al. (2011a, b), Phan et al. (2014), Saini et al. (2015), Cai et al. (2017)
Rye straw	30.9–35	21.5–30	16–25.3	Sun and Cheng (2005), Garcia-Cubero et al. (2009), Sanchez (2009)

(continued)

Table 4 (continued)

Agro residues	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Sorghum straw	2.0–35.0	24.0–27.0	15.0–21.0	Cai et al. (2017)
Sorted refuse	60	20	20	Bilal et al. (2017a, b)
Tamarind kernel	10–15	55–65		Bilal et al. (2017a, b)
Tobacco stalk	42.4	28.2	27	Dhyani and Bhaskar (2017)
Wheat bran	10.5–14.8	35.5–39.2	8.3–12.5	Bilal et al. (2017a, b)
Wheat shell	10–15	30	4–8	Bertero et al. (2012)
Wheat straw	29–49	22.3–50	5–21	Mani et al. (2006a, b), McKendry (2002), Ballesteros et al. (2006), Butler et al. (2013), Saini et al. (2015), Bharathiraja et al. (2017), Cai et al. (2017), Gaurava et al. (2017)

6.1 Survey on Crop Residue Assessment

A survey is compulsory to know about the availability, surplus, price, bulk straw handling machinery and current disposal methods for straw management. It also gave a clear-cut idea about access points for straw collection and work out estimate for the cost involved for feedstock supply and logistics. The details may be collected by interview methods and compiled to generate the biomass database for the survey region.

6.2 Feedstock Collection via Contract Farming

In order to obtain the agro residues in continuous manner and control the feedstock price, contract farming may be followed. Sugar industry is the best example for contract farming to get the assured feedstocks collected from the contracted farmers. This kind of arrangement would help to run the sugar industry in continuous manner and to sustain the market by supplying the sugar to their consumers.

6.3 Policy for Promoting Biorefinery

Straw burning in the field would lead to air/land pollution and create a negative impact on the environment. Generally, countries announced that straw burning is

illegal and implemented strict laws to prohibit the straw burning. Recently, Indian government formulated a national policy for management of crop residues (NPMCR) and implemented to stop the burning residues in the field and to promote different uses of their residues to make bequests or pellets for industrial uses (State of Indian Agriculture 2015).

6.4 Good Supply Chain and Logistics

This stage is involved in harvest and transport the straw from the paddy field to biorefinery unit, since the straw belongs to low bulk density materials, which occupies more space for storage and also involves higher transport cost. To address these issues, the harvested straw may be baled and stocked in the field. The moisture content of the feedstock is not a problem when it is used for biomass pretreatment. In order to store it in the continued area, straw may be powdered and then briquetted. This will reduce storage space, transport cost and also ease in handling the materials. The argument for the higher cost involved for briquetting process may be overruled by the cost involved for raw material handling both transport and storage area.

7 Case Study: Paddy Straw a Potential Feedstock for Biorefinery

In paddy processing, straw left in the field after harvesting of paddy grain is referred as primary agro residue. Paddy husk is obtained in the further processing of paddy grains to rice, and this husk is referred as secondary agro residues (Fig. 4). This straw contains three major components, viz. cellulose, hemicellulose and lignin. It is the largest source of lignocellulosic feedstock generated from the paddy crop.

Global paddy straw production per year is about 731 million tonnes with a major share of 91.30% by Asia (Binod et al. 2010).

Theoretical estimation of paddy straw and rice husk produced in India is about 157 and 21 million tonnes, respectively. Presently, the paddy straw has wide applications such as fodder, manure, roofing materials, fiberboard, etc. (Fig. 5). Paddy husk also often used to generate the heat energy for thermal applications. Burning/combustion is the most popular method for quick disposal of the paddy straw. According to Singh et al. (2008a, b, c), paddy straw production is ca. 17 million tonnes in Punjab alone, and in situ burning is practiced for 90% of this waste. The two in situ burning methods of the straw at site practicing by farmers are partial burning and complete burning. Farmers preferred to adopt complete burning at the agricultural field for low-cost quick disposal method. Burning is a temporary solution for disposal of huge amount of paddy straw. It simultaneously creates health problems due to worst air quality and also destroying on microorganisms in the soil. The problems associated with the



Fig. 4 Primary (paddy straw) and secondary agro residues (paddy husks) produced in harvesting and processing of paddy crop

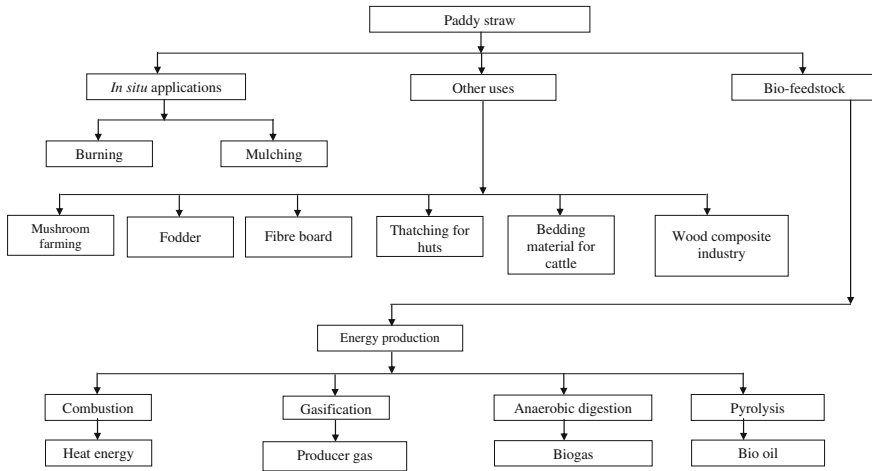


Fig. 5 Conventional disposal and energy recovery methods used for the paddy straw

handling of paddy straw are as follows: (i) transportation is a big issue, (ii) requires more space for transport and storage due to low bulk density (Fig. 6), (iii) leads to increase in transport cost and (iv) indirectly increases the feedstock price. To reduce the hurdles faced in handling, transport and storage, baling or chopping of straw was the best method. The bulk density of loose straw, hammer milled and baled straw is 20–40, 20–100 and 110–200 kg/m³, respectively (Sokhansanj and Hess 2009; Kargbo et al. 2010).

The most attractive and viable option for valorizing agro residues is biorefining. The paddy straw-based biorefinery scheme is presented in Fig. 7a–c. In comparison with biochemical the thermochemical route, it was found that the latter method leads to less productive in terms of biochemicals production. The biochemical route can be used as feedstock for production of multiple bioproducts such as bioethanol/butanol, biochemical and biocomposite materials or fuel. Among the thermochemical conversion process, the combustion and pyrolysis cannot be suitable for biorefinery approach if they used at the first stage of biorefinery conversion. The combustion of the plant wastes produces only heat and ashes. The yields of pyrolysis of straw can be in the forms of oil/solid/gas, which depends on reaction time, temperature and heating rate used in the process. Agglomeration, deposits formulation, fouling, corrosion issues and wear and tear of equipment are closely associated with the presence of mineral elements in lignocellulosic waste via thermochemical conversion method. To overcome these issues, the element should be extracted and reused (Dodson et al. 2013). Biomass pretreatment is used to break the lignin barrier and improve the enzymes accessibility of sugars. Biomass pretreatment of paddy straw is an inevitable process in the biochemical conversion route focused on bioalcohol (bioethanol or biobutanol) production. At the end of pretreatment process, hydrolysate, pretreated biomass and soluble lignin are produced. The pretreated straw contains higher cellu-



Fig. 6 Paddy straw transported from the agricultural field to the storage yard

lose content which should undergo enzymatic hydrolysis to yield fermentable sugars, and further, it was fermented to produce bioethanol. Hydrolysate can be used to produce chemicals with help of suitable microbial strain. The separated lignin can be used as feedstock for chemicals production or can be used as fuel due to its higher calorific value.

8 Conclusion

Agro residues are unavoidable by-products generated in the agricultural crop production. The annual agro residues generation is gradually increased to meet the food requirement of ever increasing world population. The major reasons for the farmers forced to adopt the onsite burning of agro residues are short period for land preparation for next crop cultivation, less straw price and higher transport charges. Valorization of single feedstock for single product production is not an economically viable project for agro residues. To reduce the environmental impacts of onsite stubble burning, biorefinery is a viable option to fractionating multiple products from these residues. Application of biorefinery approach for heterogeneous compositions of agro residues involves more challenges in selection process design and combining

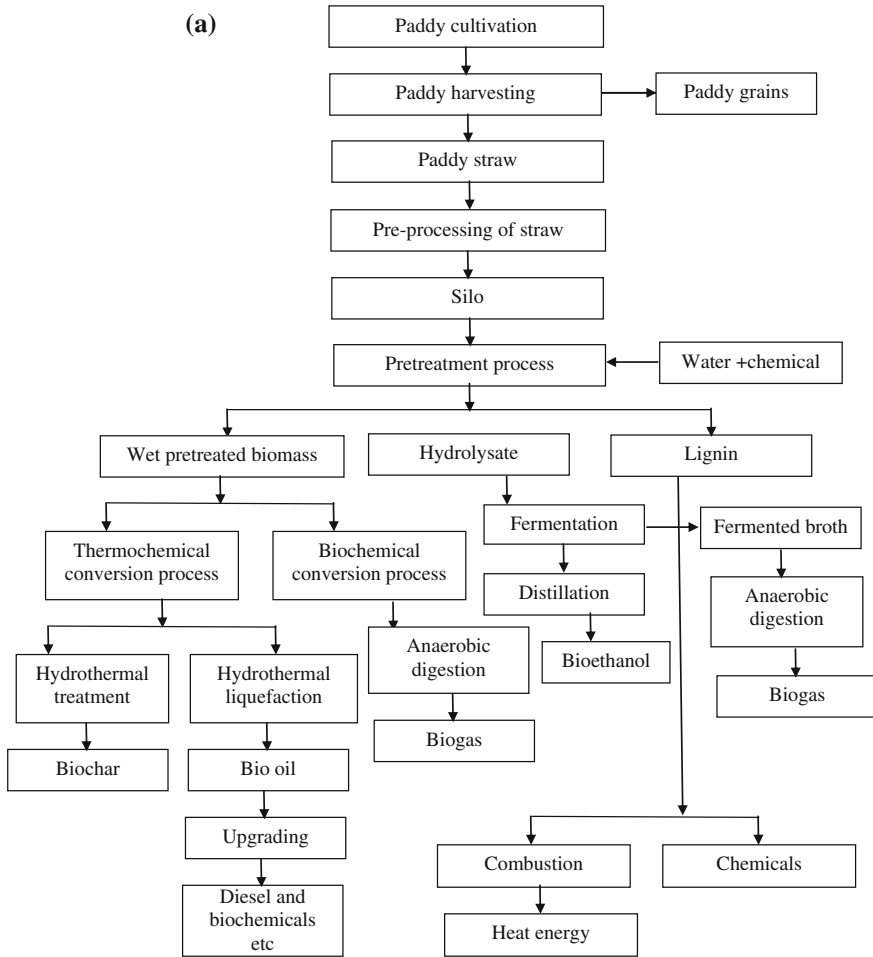


Fig. 7 a Biochemical conversion of straw into biofuel production. **b** Thermochemical conversion of straw into biofuel production. **c** Bio- and thermochemical conversion of straw into biofuel and biochemicals production

different biomass conversion technologies. The paddy straw is underutilized potential candidate to produce the bioethanol and value-added chemicals via biorefinery approach. Successful implementation of paddy straw-based biorefinery industries is depended not only on usage of technically economically viable technologies and but also on good supply chain management. Establishment of paddy straw biorefinery industries in India would lead to support the nation’s energy security, sustainability and safe disposal of huge amount of waste.

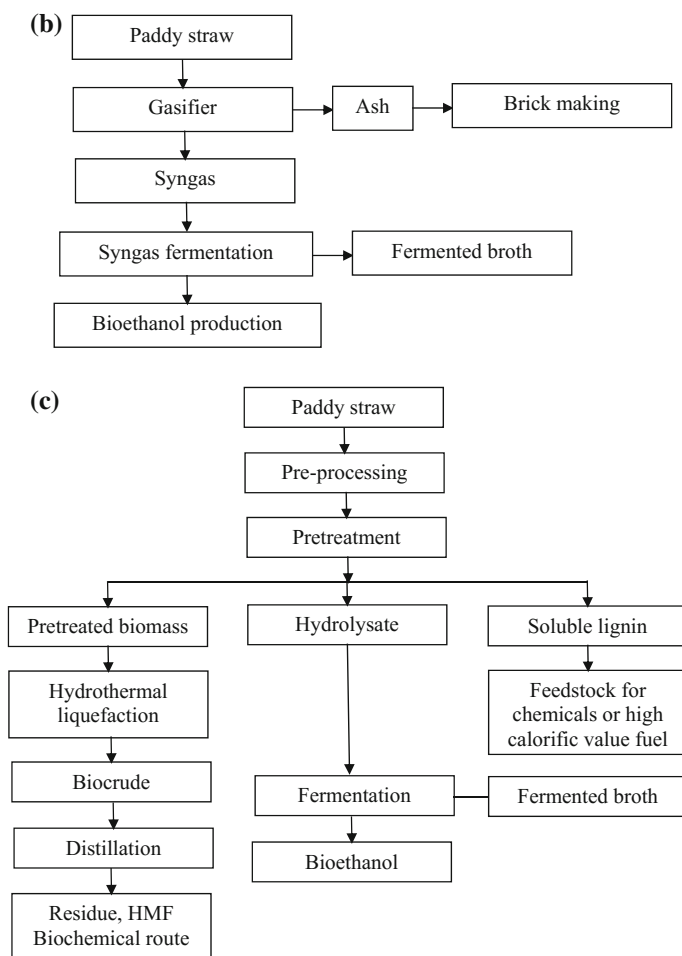


Fig. 7 (continued)

References

- Adney WS, Rivard CJ, Ming SA, Himmel ME (1991) Anaerobic digestion of lignocellulosic biomass and wastes. Cellulases and related enzymes. *Appl Biochem Biotechnol* 30:165–183
- Ahring BK, Westermann P (2007) Coproduction of bioethanol with other biofuels. *Adv Biochem Eng Biotechnol* 108:289–302. https://doi.org/10.1007/10_2007_067
- Asadullah M, Rahman MA, Ali MM, Motin MA, Sultan MB, Alam MR et al (2008) Jute stick pyrolysis for bio-oil production in fluidized bed reactor. *Bioresour Technol* 99:44–50
- Ballesteros I, Negro M, Oliva JM, Cabanas A, Manzanares P, Ballesteros M (2006) Ethanol production from steam explosion pretreated wheat straw. *Appl Biochem Biotechnol* 130:278–288
- Beller HR, Lee TS, Katz L (2015) Natural products as biofuels and bio-based chemicals: fatty acids and isoprenoids. *Nat Prod Rep* 32:1508–1526. <https://doi.org/10.1039/c5np00068h>

- Bertero M, de la Puente G, Sedran U (2012) Fuels from bio-oils: bio-oil production from different residual sources, characterization and thermal conditioning. *Fuel* 95:263–271
- Bharathiraja B, Jayamuthunagai J, Sudharsanaa T, Bhargavi A, Praveenkumar R, Chakravarthy M, Yuvaraj D (2017) Biobutanol—an impending biofuel for future: a review on upstream and downstream processing techniques. *Renew Sustain Energy Rev* 68:788–807
- De Bhowmick G, Sarmah AK, Sen R (2018) Lignocellulosic biorefinery as a model for sustainable development of biofuels and value added products. *Bioresour Technol* 247:1144–1154. <https://doi.org/10.1016/j.biortech.2017.09.163>
- Bilal M, Asgher M, Iqbal HM, Hu H, Zhang X (2017a) Biotransformation of lignocellulosic
- Bilal M, Asgher M, Iqbal HM, Hu H, Zhang X (2017b) Biotransformation of lignocellulosic materials into value-added products—a review. *Int J BiolMacromol* 98:447–458
- Binod P, Sindhu R, Singhanian RR, Vikram S, Devi L, Nagalakshmi S, Kurien N, Sukumaran RK, Pandey A (2010) Bioethanol production from rice straw: an overview. *Bioresour Technol* 101:4767–4774
- Biomass Knowledge Portal. <http://biomasspower.gov.in/>. (as per May 20, 2016)
- Bouaid A, Martinez M, Aracil J (2010) Biorefinery approach for coconut oil valorisation: a statistical study. *Bioresour Technol* 101:4006–4012
- Braga RM, Melo DMA, Aquino FM, Freitas JCO, Melo MAF, Barros JMF, Fontes MSB (2013) Characterization and comparative study of pyrolysis kinetics of the rice husk and the elephant grass. *J Therm Anal Calor*. 115:1915–1920
- Butler E, Devlin G, Meier D, McDonnell K (2013) Characterisation of spruce, salix, miscanthus & wheat straw for pyrolysis applications. *Bioresour Technol* 131:202–209
- Byun J, Han J (2016) Catalytic production of biofuels (butene oligomers) and biochemicals (tetrahydrofurfuryl alcohol) from corn stover. *Bioresour Technol* 211:360–366. <https://doi.org/10.1016/j.biortech.2016.03.123>
- Cabeza A, Piqueras CM, Sobron F, Garcia-Serna J (2016) Modeling of biomass fractionation in a lab-scale biorefinery: solubilization of hemicellulose and cellulose from holm oak wood using subcritical water. *Bioresour Technol* 200:90–102. <https://doi.org/10.1016/j.biortech.2015.09.063>
- Caglar A, Demirbas A (2001) Conversion of cotton cocoon shell to liquid products by supercritical fluid extraction and low pressure pyrolysis in the presence of alkalis. *Energy Convers Manage* 42:1095–1104
- Cai J, He Y, Yu X, Banksb Scott W, Yang Y, Zhang X, Yu Y, Liu R, Bridgwater Anthony V (2017) Review of physicochemical properties and analytical characterization of lignocellulosic biomass. *Renew Sustain Energy Rev* 76:309–322
- Chen D, Cen K, Jing X, Gao J, Li C, Ma Z (2017) An approach for upgrading biomass and pyrolysis product quality using a combination of aqueous phase bio-oil washing and torrefaction pretreatment. *Bioresour Technol* 233:150–158. <https://doi.org/10.1016/j.biortech.2017.02.120>
- Chen WH, Pen BL, Yuz CT, Hwang WS (2011a) Pretreatment efficiency and structural characterization of rice straw by an integrated process of dilute-acid and steam explosion for bioethanol production. *Bioresour Technol* 102:2916–2924
- Chen WH, Pen BL, Yu CT, Hwang WS (2011b) Pretreatment efficiency and structural characterization of rice straw by an integrated process of dilute-acid and steam explosion for bioethanol production. *Bioresour Technol* 102:2916–2924
- Chen G, Yao J, Yang H, Yan B, Chen H (2015) Steam gasification of acid-hydrolysis biomass CAHR for clean syngas production. *Bioresour Technol* 179:323–330. <https://doi.org/10.1016/j.biortech.2014.12.039>
- Christopher M, Mathew AK, Kiran Kumar M, Pandey A, Sukumaran RK (2017) A biorefinery-based approach for the production of ethanol from enzymatically hydrolysed cotton stalks. *Bioresour Technol* . <https://doi.org/10.1016/j.biortech.2017.03.190>
- de Jong E, Jungmeier G (2015) Biorefinery concepts in comparison to petrochemical refineries. In: *Industrial biorefineries & white biotechnology*, pp 3–33
- Dhyani V, Bhaskar T (2017) A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew Energy*

- Diaz AB, Moretti MMD, Bezerra-Bussoli C, Nunes CDCC, Blandino A, da Silva R et al (2015) Evaluation of microwave-assisted pretreatment of lignocellulosic biomass immersed in alkaline glycerol for fermentable sugars production. *Bioresour Technol* 185:316–323
- Dodson JR, Li X, Zhou X, Zhao K, Sun N, Atahan P (2013) Origin and spread of wheat in China. *Quatern Sci Rev* 72:108–111
- Dominguez E, Romani A, Alonso JL, Parajo JC, Yanez R (2014) A biorefinery approach based on fractionation with a cheap industrial by-product for getting value from an invasive woody species. *Bioresour Technol* 173:301–308. <https://doi.org/10.1016/j.biortech.2014.09.104>
- ECN - Phyllis2 Database for biomass and waste (www.ecn.nl/phyllis2)
- Esteghlalian A, Hashimoto AG, Fenske JJ, Penner MH (1997) Modeling and optimization of the dilute sulfuric acid pretreatment of corn stover, poplar and switchgrass. *Bioresour Technol* 59:129–136
- Eynde EV, Lenaerts B, Tytgat T, Blust R, Lenaerts S (2016) Valorization of flue gas by combining photocatalytic gas pretreatment with microalgae production. *Environ Sci Technol* 50:2538–2545. <https://doi.org/10.1021/acs.est.5b04824>
- Friedl A, Padouvas E, Rotter H, Varmuza K (2005) Prediction of heating values of biomass fuel from elemental composition. *Anal Chim Acta* 544:191–198
- Gao H, Chen X, Wei J, Zhang Y, Zhang L, Chang J et al (2016) Decomposition dynamics and changes in chemical composition of wheat straw residue under anaerobic and aerobic conditions. *PLoS ONE* 11(7):e0158172
- Garcia-Cubero MT, González-Benito G, Indacochea I, Coca M, Bolado S (2009) Effect of ozonolysis pretreatment on enzymatic digestibility of wheat and rye straw. *Bioresour Technol* 100:1608–1613
- Gaurava N, Sivasankarib S, Kiranc GS, Ninawea A, Selvinb J (2017) Utilization of bioresources for sustainable biofuels: a review. *Renew Sustain Energy Rev* 73:205–214
- Hellier P, Purton S, Ladommatos N (2015) Molecular structure of photosynthetic microbial biofuels for improved engine combustion and emissions characteristics. *Front Bioeng Biotechnol* 3:49. <https://doi.org/10.3389/fbioe.2015.00049>
- Henry RJ (2018) Biofuels from crop plants. *Encyclopedia of applied plant sciences*, 2nd edn, vol 3, pp 177–179. <http://dx.doi.org/10.1016/B978-0-12-394807-6.00169-6>
- Hiloidhari M, Baruah D (2011a) Crop residue biomass for decentralized electrical power generation in rural areas (part 1): investigation of spatial availability. *Renew Sustain Energy Rev* 15:1885–1892
- Hiloidhari M, Baruah DC (2011b) Rice straw residue biomass potential for decentralized electricity generation: a GIS based study in Lakhimpur district of Assam, India. *Energy Sustain Dev* 15:214–222
- Hiloidhari M, Das D, Baruah DC (2014) Bioenergy potential from crop residue biomass in India. *Renew Sustain Energy Rev* 32:504–512
- IARI (2012) Crop residues management with conservation agriculture: potential, constraints and policy needs. Indian Agricultural Research Institute, New Delhi, vii + 32 p
- Jekayinfa SO, Scholz V (2009) Potential availability of energetically usable crop residues in Nigeria. *Energy Sources Part A Recovery Utilization Environ Eff* 31:687–697
- Kargbo F, Xing J, Zhang Y (2010) Property analysis and pretreatment of rice straw for energy use in grain drying: a review. *Agric Biol J North Am* 1(3):195–200
- Kis D, Susic B, Guberac V, Voca N, Rozman V, Sumanovac L (2009) Soybean biomass as a renewable energy resource. *Agric Conspic Sci* 74:201–203
- Laghari SM, Isa MH, Laghari AJ (2016) Delignification of palm fiber by microwave assisted chemical pretreatment for improving energy efficiency. *Malays J Sci* 35:8–14
- Le DM, Sørensen HR, Knudsen NO, Schjoerring JK, Meyer AS (2014) Biorefining of wheat straw: accounting for the distribution of mineral elements in pretreated biomass by an extended pretreatment-severity equation. *Biotechnol Biofuels* 7(1):141
- Ludueña L, Fasse D, Alvarez VA, Stefani PM (2011) Nanocellulose from rice husk following alkaline treatment to remove silica. *BioResources* 6:1440–1453

- Mani S, Tabil LG, Sokhansanj S (2006a) Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses. *Biomass Bioenergy* 30:648–654
- Mani S, Tabil LG, Sokhansanj S (2006b) Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses. *Biomass Bioenergy* 30:648–654
- McKendry P (2002) Energy production from biomass (part 1): overview of biomass. *Bioresour Technol* 83(1):37–46
- Minowa T, Kondo T, Sudirjo ST (1998) Thermochemical liquefaction of Indonesian biomass residues. *Biomass Bioenergy* 14:517–524
- Motte JC, Escudie R, Beaufils N, Steyer JP, Bernet N, Delgenes JP, Dumas C (2014) Morphological structures of wheat straw strongly impacts its anaerobic digestion. *Ind Crops Prod* 52:695–701
- National Renewable Energy Laboratory (2009) Renewable energy data book: energy efficiency & renewable energy
- Nigam PS, Gupta N, Anthwal A (2009) Pre-treatment of agro-industrial residues. In: Nigam PS, Pandey A (eds) *Biotechnology for agro-industrial residues utilization*, 1 edn. Springer, Netherlands, pp 13–33
- Nordin R, Said CMS, Ismail H (2007) Properties of rice husk powder/natural rubber composite. *Solid State Sci Technol* 15:83–91
- Octave S, Thomas D (2009) Biorefinery: toward an industrial metabolism. *Biochimie* 91:659–664
- Phan BMQ, Duong LT, Nguyen VD, Tran TB, Nguyen MHH, Nguyen LH, Nguyen DA, Luu LC (2014) Evaluation of the production potential of bio-oil from Vietnamese biomass resources by fast pyrolysis. *Biomass Bioenergy* 62:74–81
- Pilon G (2007) Utilization of Arecanut (*Areca catechu*) husk for gasification. [MSc. thesis]. Department of Bioresource Engineering, McGill University, Montreal
- Prasad S, Singh A, Joshi HC (2007a) Ethanol as an alternative fuel from agricultural, industrial and urban residues. *Resourc Conserv Recycl* 50:1–39
- Prasad S, Singh A, Joshi HC (2007b) Ethanol as an alternative fuel from agricultural, industrial and urban residues. *Resourc Conserv Recycl* 50:1–39
- Rahman MT (2006) Green energy development model in the St.Martin's Island and energy from coconut palm biomass, ISBN: 984-8323-02-3
- Rai SN, Walli TK, Gupta BN (1989) The chemical composition and nutritive value of rice straw after treatment with urea or *Coprinus fimetarius* in a solidstate fermentation system. *Anita Feed Sci Technol* 26:81–92
- Raman S, Mohr A, Helliwell R, Ribeiro B, Shortall O, Smith R, Millar K (2015) Integrating social and value dimensions into sustainability assessment of lignocellulosic biofuels. *Biomass Bioenergy* 82:49–62. <https://doi.org/10.1016/j.biombioe.2015.04.022>
- Raveendran K, Ganesh A, Khilar C (1995) Influence of mineral matter on biomass pyrolysis characteristics. *Fuel* 74:1812–1822
- Saini JK, Saini R, Tewari L (2015) Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments. *Biotech* 5:337–353
- Sanchez C (2009) Lignocellulosic residues: biodegradation and bioconversion by fungi. *Biotechnol Adv* 27:185–194
- Sarnklong C, Cone JW, Pellikaan W, Hendriks WH (2010) Utilization of rice straw and different treatments to improve its feed value for ruminants: a review. *Asian Aust J Anim Sci* 23(5):680–692
- Singh G, Ahuja N, Batish M, Capalash N, Sharma P (2008a) Biobleaching of wheat straw-rich soda pulp with alkalophilic laccase from gamma-proteobacterium JB: optimization of process parameters using response surface methodology. *Bioresour Technol* 99:7472–7479. <https://doi.org/10.1016/j.biortech.2008.02.023>
- Singh J, Panesar BS, Sharma SK (2008b) Energy potential through crop biomass using geographical information system—a case study of Punjab. *Biomass Bioenergy* 32:301–307
- Singh RP, Dhaliwal HS, Sidhu HS, Manpreet-Singh YS, Blackwell J (2008c) Economic assessment of the Happy Seeder for rice-wheat systems in Punjab, India. In: Conference Paper, AARES 52nd Annual conference. ACT, Canberra. Australia

- Sokhansanj S, Hess JR (2009) Biomass supply logistics and infrastructure. In: *Biofuels*, Humana Press, Totowa, NJ, pp 1–25
- State of Indian Agriculture (2015–2016) Ministry of Agriculture & Farmers Welfare, Government of India
- Sun Y, Cheng JJ (2005) Dilute acid pretreatment of rye straw and Bermuda grass for ethanol production. *Bioresour Technol* 96:1599–1606
- Tao L, Aden A, Elander RT (2013) Economics of pretreatment for biological processing. In: *Aqueous pretreatment of plant biomass for biological and chemical conversion to fuels and chemicals*. Wiley, Hoboken, pp 311–333. <https://doi.org/10.1002/9780470975831.ch15>
- Thomas P, Soren N, Rumjit NP, James JG, Saravanakumar MP (2017) Biomass resources and potential of anaerobic digestion in Indian scenario. *Renew Sustain Energy Rev* 77:718–730
- WBA Global Bioenergy Statistics (2017). www.worldbioenergy.org. (accessed on 31.1.2018)
- Wang MJ, Huang YF, Chiueh PT, Kuan WH, Lo SL (2012) Microwave-induced torrefaction of rice husk and sugarcane residues. *Energy* 37:177–184
- Wilaipon P (2009) The effects of briquetting pressure on banana-peel briquette and the banana waste in Northern Thailand. *Am J App Sci* 6:167–171
- World Energy Outlook (2002) International Energy Agency, IEA/OECD, Paris
- Xu J, Xiong P, He B (2016) Advances in improving the performance of cellulase in ionic liquids for lignocellulose biorefinery. *Bioresour Technol* 200:961–970. <https://doi.org/10.1016/j.biortech.2015.10.031>
- Zabaniotou A, Ioannidou O, Antonakou E, Lappas A (2008) Experimental study of pyrolysis for potential energy, hydrogen and carbon material production from lignocellulosic biomass. *Int J Hydrogen Energy* 33:2433–2444
- Zhang M, Xie L, Yin Z, Khanal SK, Zhou Q (2016) Biorefinery approach for cassava-based industrial wastes: current status and opportunities. *Bioresour Technol* 215:50–62. <https://doi.org/10.1016/j.biortech.2016.04.026>