Environment and Ecology 41(2B) : 1122–1127, April– June 2023
ISSN 0970-0420

Bio-Refinery- A Novel Strategy to Advocate Sustainability-A Review

Arunima Babu C. S., Sheeja K. Raj, Dhanu Unnikrishnan

Received 25 November 2022, Accepted 21 March 2023, Published on 21 June 2023

ABSTRACT

The world is currently facing severe energy crisis due to incessant increase in energy demands and depletion of fossil fuels. Besides, there is an increasing perception of the end of cheap fossil era. Therefore, there is an urge of shifting dependency from finite fossil fuels to renewable resources. Agricultural waste is a huge pool of untapped bio- mass resources, that can be converted to bio-energy and bio-based products. The idea of manufacturing the energy rich bio- based products are analogous to integrated petroleum refinery, commonly known as bio-refinery.

Keywords First Generation bio-refinery, Lignocellulosic bio-mass, Second Generation bio-refinery, third generation bio-refinery.

Arunima Babu C. S.[1], Dhanu Unnikrishnan[3]
[1,3]PhD Scholar
Department of Agronomy, College of Agriculture, Vellayani 695522, Kerala Agricultural University, India

Sheeja K. Raj[2]*
[2]Assistant Professor (Agronomy)
Department of Organic Agriculture, College of Agriculture, Vellayani 695522, Kerala Agricultural University, India

Email: sheeja.raj@kau.in
*Corresponding author

INTRODUCTION

The food and energy security of the globe is inevitable for the viability of human civilization. The increase in energy demands and exhaustion of fossil fuels have caused severe energy crisis around the world. In addition, the escalating cost of fuels coupled with climate change, pollution and loss of bio-diversity has called for the need of alternative resources. Among the energy sources, bio-mass resources are extremely promising since they are widespread and cheaply available in most of the countries. To enhance the resource utilization efficiency and manage organic wastes in primary production, bio-refinery is of supreme prominence to promote sustainability, environmental and food security.

Bio-refinery

The term "Bio-refinery" was introduced in 1990 by the National Renewable Energy Laboratory. The bio-refinery concept embraces broader scale of technologies that are capable to discrete bio-mass resources into its components and to value-added products, bio-fuels, and chemicals. Bio-refineries encompasses with the usage of bio-mas and its conversion to fuels, heat, electricity, high-value chemicals and other bio-based products (Kumar and Yaashikaa 2020).

Bio-mass is the bio-residue derived from living or dead plant parts of forestry, agriculture and water-based flora (Kumar *et al.* 2020). The various bio-mass resources available are agricultural residues, animal waste, household waste, aquatic bio-mass, forest wood, saw dust and energy crops.

Development of closed-loop bio-refineries that ensure sustainability and economic viability through complete use of bio-mass, minimal waste and generation of energy rich products from available sources forms the bio-refinery system. This results in increase in profitability and competitiveness over petrochemical equivalents. Choudhary *et al.* (2018) classified bio-refinery based on the origin and type of feedstock as first-generation (1G) bio-refinery, second-generation (2G) bio-refinery and third-generation (3G) bio-refinery.

First generation (1g) bio-refinery

The source of raw materials in the first-generation bio-refineries consists of the sugar or starch portion of cereals and tuber crops and seeds of oilseed crops (Rutz and Janssen 2007). The starch crops undergo mechanical fractionation, hydrolysis and fermentation for the production of bio-ethanol and animal feed. Whereas the procedural steps for bio-diesel are pressing, oil extraction and esterification of oilseed crops (Cherubini *et al.* 2010). Prasad *et al.* (2007) reported that among the different bio-fuel production systems, average net energy production (GJ ha^{-1} yr^{-1}) from palm oil recorded significantly highest value. It was also reported that the average greenhouse gases (GHG) emissions from the bio-fuel production systems (g CO_2 eq. MJ^{-1}) was significantly lower than conventional gasoline and diesel.

Despite of the elevated production of bio-fuel and other energy rich value-added products, first-generation bio-refineries became unnoticeable due to its dependence on edible reserves. This type of bio-refineries created a food versus energy conflict (Agbor *et al.* 2011). In India, 5×10^8 t of agricultural residues are generated annually (Sarsaiya *et al.* 2019). Therefore, exploring the potential of non-edible lignocellulosic residues led to the advancement of second-generation bio- refinery.

Second generation (2g) bio-refinery

Lignocellulosic bio-mass is a potential renewable source of energy to mitigate the global climate change. The monetary value of the bio-mass residues can be maximized by converting into useful bio-materials in an integrated manner, thereby reducing the waste piles liberated (Thomsen 2005). Besides, it can ensure energy security of the rural economy. But, cost effective methods of converting lignocellulosic residues into bio- fuel and other high priced products are laborious, due to the complex framework and obstinance of lignocellulose.

Lignocellulosic bio-mass can be grouped into agricultural residues (straw, bagasse stover), energy crops, aquatic flora and forest (Zabed *et al.* 2017). The important constituents of lignocellulosic bio-mass are cellulose, hemicellulose and lignin (Menon and Rao 2012). Based on the type of bio-mass, amount of cellulose, hemicellulose and lignin varies (Table 1).

The bio-mass is converted to energy by thermochemical and bio-chemical/bio-logical processes (Bhuyan *et al.* 2019). The thermal conversion technologies consist of a series of steps viz., pyrolysis, bio-mass gasification, combustion, and liquefaction. Thermochemical conversion processes are advantageous than bio-chemical conversion techniques with regard to the flexibility, time of reaction and potential to use all types of bio-mass.

Bio-conversion of lignocellulosic bio-mass into ethanol includes a series of steps viz., pre-treatment

Table 1. Fractions of major components in lignocellulosic bio-mass.

Bio-mass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Corn stover	39	25	13	Saini *et al.* 2015
Sugarcane bagasse	45	22	31	Kim and Day 2011
Rice straw	34	25	13	Saini *et al.* 2015
Wheat straw	35	28	18	Saini *et al.* 2015
Cotton	90	10	0	Menon and Rao 2012

and fractionation of bio-mass, generation of lytic enzymes, enzymatic hydrolysis of pre-treated bio-mass, microbial fermentation and downstream processing (Patel and Shah 2021). Pre-treatment is an inevitable process for the breakdown of tightly interlinked matrix of lignocellulose. For the subsequent hydrolytic processes, removal of lignin, hydrolysis of hemicellulose and reduction of cellulose are necessary to make the bio-mass more amenable to release fermentable sugars (Sukumaran *et al.* 2017). Among the different pre-treatment methods, steam explosion by saturated steam (483 K and 0.69 to 4.83 MPa) for 5 minutes undergoes hydrolysis of 80-100% of hemicellulose (Maity *et al.* 2014).

Conversion of cellulose and hemicellulose in the presence of enzymes is the bottleneck in usage of bio-mass for the production of bio-fuel and other high valued products. A combination of enzymes viz., endoglucanases, exoglucanses and glucosidases are essential for the total hydrolysis of cellulose to glucose (Saini *et al.* 2015). Hemicellulases like xylanase, mannanase, arabinose, mannosidase and xylosidase (main-chain-cleaving enzymes) and esterases, L–arabinofuranosidase (side-chain- cleaving enzymes) increase the cellulose accessibility by solubilizing hemicelluloses. Lignolytic enzymes like laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP), play a pivotal role in the removal of lignin and facilitating enzymatic saccharification of bio-mass (Chukwuma *et al*. 2020).

Several fermentation processes are available for the production of 2G ethanol from lignocellulosic bio-mass. Micro-organisms like *Saccharomyces cerevisiae,* ferments hexoses to ethanol efficiently. Xylose-fermenting yeasts (*Candida tropicalis, Candida shehatae*), filamentous fungi (*Fusarium oxysporum, Rhizopus oryzae* and *Mucor circinelloides*) and ethanologenic xylose-fermenting bacteria (*Klebsiella oxytoca* and *Escherichia coli*) aids in xylose fermentation (Komeda *et al.* 2014).

Among the different types of fermentation processes, batch process and fed-batch process are commonly preferred due to lesser contamination and higher ethanol yield. For fed batch process, the feeding time is 4–6 hours and fermentation time of 6–10 hours.

A normal E10 blend (10% ethanol blend with gasoline) reduce GHG emissions, fossil energy use and petroleum use by 2, 3 and 6% respectively (Chen and Fu 2016).

Production of 2G ethanol from lignocellulosic bio-mass has increased despite of the challenges which obstructs the progress of cost effective production of ethanol. The world wide trend in production of ethanol showed that the leading producers are USA followed by Brazil and European Union (RFA 2020).

Government initiatives for 2G ethanol

Pradhan Mantri JI-VAN Yojana, provides financial outlay of Rs 1969.50 crore (2018-19 to 2023-24) to 12 integrated bio-ethanol projects using lignocellulosic bio-mass and other renewable sources. Another important initiative was Ethanol Blended Petrol (EBP) program which aims to attain 10% and 20% ethanol blending in petrol by 2021-22 and 2030 respectively.

Bio-refining energy crops

In the recent future, the lignocellulosic C4 crops *Miscanthus sinensis* (silver grass) and *Panicum virgatum* (switch grass), are likely to outcompete *Saccharum officinarum.* Silver grass and switch grass have a potential to produce 2960 gal ha^{-1} and 1040 gal ha^{-1} of ethanol from 29.6 Mg ha^{-1} and 10.4 Mg ha^{-1} of biomass respectively (Heaton *et al.* 2008). Compared to other bio-mass sources, C4 grasses may be able to produce more than double the annual bio-mass yield in warm and temperate regions due to its photosynthetic pathway (Reijnders 2010).

***Pontederia crassipes* as a potential bio-fuel crop**

Pontederia crassipes was introduced from South America to India in 1896, as an ornamental crop. However, it was discovered that it could be sustainably managed in its natural ecosystem and used in bio-fuel production (i.e., bio-ethanol and bio-gas). Water hyacinth has low lignin (10%) and higher amounts of cellulose (20%) and hemicellulose (33%) (Gunnarsson and Petersen 2007). Because of the low lignin content in water hyacinth, cellulose and hemicellulose fraction can be easily transformed into

Table 2. Hemi-cellulose based value added products.

Value added product	Application	Reference
Lactic acid	Pharmaceuticals, chemicals compounds and bio-polymers	(Abdel-Rahman and Sonomoto 2016)
Xylitol	low-calorie sweetener in toothpastes, chewing gums, anti-diabetic products and against dental problems	(Irmak *et al.* 2017)
Xylooligosaccharides	Prebio-tic activity and health benefits to humans and animals. Antioxidant and anti-allergicproperties. Control obesity, lipid and glucose homeostasis, insulin sensitivity, control diabetes, and in cure of gastrointestinal infections	(Jain *et al.* 2015)
Polyhydroxyalkanoates	Compostable bio-based polyesters, for integrated bio-refinery	(Snell and Peoples 2009)
Furfural	Preparation of inks, adhesives, nematicides, fertilizers, fungicides and flavoring compounds	(Raman and Gnansounou 2015)

fermentable sugar and consequently to energy rich products (Bhattacharya and Kumar 2010).

Bio-diesel

Bio-diesel is derived from renewable resources like vegetable oils or animal fats and short chain alcohols, through trans-esterification reaction (Fukuda *et al.* 2001) In this reaction ester is converted into a mixture of fatty acids esters which is purified to obtain bio-diesel. A basic, acidic or enzymatic catalyst can be used to accelerate the reaction. Since cost is the major concern in bio-diesel production, use of non-edible vegetable oils in presence of basic, acidic or enzymatic catalyst have been studied for several years.

Value added products

Hemicellulose-based value added products

During pre-treatments like acid hydrolysis and steam explosion, hemicelluloses are prone to degradation and is considered as the most underutilized fraction during the bio-conversion of lingo-cellulosic biomass to ethanol. The list of hemicellulose based value added products are given in Table 2.

Among the value added products from lignin, vanillin is the most important product. It is most widely used as a flavoring agent. Besides, it is used for the production of polymers viz., poly-vanillin, hydrogels and polyethylene. Vanillin alcohol is used for the production of plastics and polyesters (Ahmad and Pant 2018).

Bio-plastic production from renewable lignocellulosic feedstocks

Heavy use of plastic products had adverse impact on mammalian health and environment (Thompson *et al.* 2009). There is growing attention to boost the growth of bio- plastics, which hampers several benefits over petroleum derived plastics, like low greenhouse gas emission and bio-degradation.

Ligno-cellulosic materials have huge potential to develop eco-friendly bio-plastic because of their abundance, non-edible nature and renewability (Deepa *et al.* 2019). Both lignin and cellulose materials can be easily converted to bio-plastics through surface modifications and chemical conversions processes. Polylactic acid, polyhydroxyalkanoates, polyurethanes, bio-polyethylene and starch based bio-plastics are the common bio-based plastics generated from lignin and cellulose (Reshmy *et al.* 2021).

Third generation (3g) bio-refinery

Microalgae can be used as a bio-fuel feedstock in successfully handling the energy chaos, climate change and natural resource decrement (Chew *et al.* 2017). It is a storehouse of proteins, lipids and carbohydrates. Lipids from microalgae can be extracted and used as potential feedstock for producing bio-diesel. Micro algal carbohydrates act as the main source of carbon in fermentation processes to substitute conventional carbohydrate sources such as simple sugars. Some long chain fatty acids present in microalgae are utilized as food supplements, whereas, pharmaceutical value have been identified in several proteins and pigments (Yen *et al.* 2013). An oil content of at least 20-50% is seen in microalgae viz., *Botryococcus braunii, Chlorella* sp.

Nannochloris sp. Khoo *et al.* (2013) reported that starch and cellulose derived from algal biomass through mechanical bob or enzyme hydrolysis are used for the production of bio-ethanol. Algae can grow on non-arable lands and do not change land usage. Carbon dioxide produced in industrial flue gases is also used in the production of algal biomass. Fresh water is not an essential requirement for algal biomass cultivation. Waste water from industrial and domestic sewage can be used for its cultivation. The major hurdle between production and commercialization of algal bio- fuels is the cost incurred in processing algal biomass. Harvesting corresponds to about 20-30% of total cultivation costs.

CONCLUSION

Bio-refinery offers many opportunities for the production of an array of fuels and organic chemicals from bio-mass. It is an ecofriendly and sustainable way to manufacture marketable bio-based products, similar to the petro-based refinery. Bio- refinery could emerge as a new epitome of circular bio-economy, by comprehensively emphasizing the major aspects of sustainability.

REFERENCES

Abdel-Rahman MA, Sonomoto K (2016) Opportunities to overcome the current limitations and challenges for efficient microbial production of optically pure lactic acid. *J Biotechnol*. 236: 176-192.

Agbor VB, Cicek N, Sparling R, Berlin A, Levin DB (2011) Biomass pretreatment: Fundamentals toward application. *Biotechnol Adv* 29(6): 675-685.

Ahmad E, Pant KK (2018) Lignin conversion: A key to the concept of lignocellulosic biomass-based integrated biorefinery. In: Waste Biorefinery. Elsevier, pp 409-444.

Bhattacharya A, Kumar P (2010) Water hyacinth as a potential biofuel crop. *J Environ Agric Food Chem* 9(1): 112-122.

Bhuyan N, Sut D, Gogoi L, Kataki R, Goud VV (2019) Rural biorefinery: A viable solution for production of fuel and chemicals in rural India. In: Sustainable Bioenergy. Elsevier, pp 21-47.

Chen H, Fu X (2016) Industrial technologies for bioethanol production from lignocellulosic biomass. *Renewable Sustain Energy Rev* 57: 468-478.

Cherubini F, Nain L, Ulgiati S (2010) Crop residues as raw materials for bio-refinery systems–A LCA case study. *Appl Energ* 87(1): 47-57.

Chew KW, Yap JY, Show PL, Suan NH, Juan JC, Ling TC, Lee DJ, Chang JS (2017) Microalgae biorefinery: High value products perspectives. *Biores Technol* 229: 53-62.

Choudhary J, Singh S, Nain L (2018). Bio prospecting thermo tolerant ethanologenic yeasts for simultaneous saccharifi cation and fermentation from diverse environments. *J Biosci Bioeng* 123(3): 342-346.

Chukwuma OB, Rafatullah M, Tajarudin HA, Ismail N (2020) Lignocellulolytic enzymes in biotechnological and industrial processes: A review. *Sustain* 12(18): 7282-7285.

Deepa B, Chirayil CJ, Pothan LA, Thomas S (2019) Lignocellulose-based nanoparticles and nanocomposites: Reparation, properties, and applications. In: Lignocellulose for Future Bioeconomy. Elsevier, pp 41-69.

Fukuda H, Kondo A, Noda H (2001) Biodiesel fuel production by transesterification of oils. *J Biosci Bioeng* 92(5): 405-416.

Gunnarsson CC, Petersen CM (2007) Water hyacinths as a resource in agriculture and energy production: A literature review. *Waste Manag* 27(1): 117-129.

Heaton EA, Flavell RB, Mascia PN, Thomas SR, Dohleman FG, Long SP (2008) Herbaceous energy crop development: Recent progress and future prospects .*Curr Opinion Biotechnol* 19(3): 202-209.

Irmak S, Canisag H, Vokoun C, Meryemoglu B (2017) Xylitol production from lignocellulosics: Are corn biomass residues good candidates. *Biocatalysis Agric Biotechnol* 11: 220-223.

Jain I, Kumar V, Satyanarayana T (2015) Xylooligosaccharides: An economical prebiotic from agroresidues and their health benefits. *Ind J Exp Biol* 53: 131-142.

Khoo HH, Koh CY, Shaik MS, Sharratt PN (2013) Bioenergy co-products derived from microalgae biomass via thermochemical conversion–life cycle energy balances and CO_2 emissions. *Biores Technol* 143: 298-307.

Kim M, Day DF (2011) Composition of sugar cane, energy cane, and sweet sorghum suitable for ethanol production at Louisiana sugar mills. *J Industrial Microbiol Biotechnol* 38(7): 803-807.

Komeda H, Yamasaki-Yashiki S, Hoshino K, Asano Y (2014) Identification and characterization of D-xylulokinase from the D-xylose-fermenting fungus. *Mucor circinelloides FEMS Microbiol Letters* 360(1): 51-61.

Kumar B, Bhardwaj N, Agrawal K, Chaturvedi V, Verma P (2020) Current perspective on pretreatment technologies using lignocellulosic biomass: An emerging biorefinery concept. Fuel Process. *Technol* 199: 196-244.

Kumar PS, Yaashikaa PR (2020) Sources and operations of waste bio-refineries, in refining biomass residues for sustainable energy and bio-products. *J Biosci Bioeng* 124 (4): 111–133.

Maity JP, Bundschuh J, Chen CY, Bhattacharya P (2014) Microalgae for third generation biofuel production, mitiga tion of greenhouse gas emissions and wastewater treatment: Present and future perspectives–A mini review. *Energy* 78: 104-113.

Menon V, Rao M (2012) Trends in bioconversion of lignocellulose: Biofuels, platform chemicals and biorefinery concept. *Progr Energy Combustion Sci* 38(4): 522-550.

Patel A, Shah A (2021) Integrated lignocellulosic biorefinery: Gateway for production of second generation ethanol and value added products. *J Biores Bioprod* 13(3): 4-43.

Prasad S, Singh A, Joshi HC (2007) Ethanol as an alternative fuel from agricultural, industrial and urban residues. *Res Conserv Recycling* 50 (1): 1-39.

Raman JK, Gnansounou E (2015) Furfural production from empty fruit bunch–A biorefinery approach. *Indus Crops Prod* 69: 371-377.

Reijnders L (2010) Transport biofuel yields from food and ligno cellulosic C4 crops. *Biomass Bioenergy* 34(1): 152-155.

Renewable Fuel Association (2020) Renewable Fuel Association – Homepage Available at: http://www.ethanolrfa.com. [4 April 2020].

Reshmy R, Thomas D, Philip E, Paul SA, Madhavan A, Sindhu R, Sirohi R, Varjani S, Pugazhendhi A, Pandey A, Binod P (2021) Bioplastic production from renewable lignocellulosic feedstocks: A review. *Rev Environ Sci Bio/Technol* 14(2): 1-21.

Rutz D, Janssen R (2007) Biofuel Technology Handbook. WIP Renewable energies, pp 95.

Saini JK, Saini R, Tewari L (2015) Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: Concepts and recent developments. *Biotechno*l 5(4): 337-353.

Sarsaiya S, Jain A, Awasthi SK, Duan Y, Awasthi MK, Shi J (2019) Microbial dynamics for lignocellulosic waste bioconversion and its importance with modern circular economy, challenges and future perspectives. *Biores Technol* 291: 121905.

Snell KD, Peoples OP (2009) PHA bioplastic: A value added coproduct for biomass biorefineries. *Biofuels Bioprod Biorefining Innov Sustain Econ* 3(4): 456- 467.

Sukumaran RK, Mathew AK, Kumar A, Chistopher M, Sankar M (2017) First and second- generation ethanol in India: A comprehensive overview on feedstock availability and potential conversion yields. *Sustain Energy Rev* 4(1): 223-246.

Thompson RC, Moore CJ, vom Saal FS, Swan SH (2009) Plastics, the environment and human health: Current consensus and future trends. *Phil Transactions Royal Soc B Biol Sci* 364(1526): 2153-2166.

Thomsen MH (2005) Complex media from processing of agricultural crops for microbial fermentation. *Appl Microbiol Biotechnol* 68(5): 598-606.

Yen HW, Hu IC, Chen CY, Ho SH, Lee DJ, Chang JS (2013) Microalgae based bio- refinery–from bio-fuels to natural products. *Biores Technol* 135(2): 166-174.

Zabed H, Sahu JN, Suely A, Boyce AN, Faruq G (2017) Bioethanol production from renewable sources: Current perspectives and technological progress. *Renewable Sustain Energy Rev* 71: 475-501.