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## De-construction of major Indian cereal crop residues through chemical pretreatment for improved biogas production: An overview



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### ABSTRACT

The expedition for inexpensive, renewable and environmentally friendly source of energy to replace the conventional sources like coal and petroleum is currently the most focused research area. Biomass resource in the form of crop residues is the abundant and readily accessible renewable resource. Wheat, rice and maize are the major cereal crops around the globe and are found to be the major sources of residual lignocellulosic biomass in the form of straw. In India, this is usually burnt in the field and is thus underutilized. These residues may be harnessed for bioenergy production by thermal and biochemical processes. This review is exclusively focused on chemical pretreatment of these residues to generate biomethane by unmasking lignin. The paper also reviews the essential properties of the residual biomass such as proximate, ultimate and compositional for the quality of derived biofuels (bioethanol and biomethane). Biomass to bioenergy conversion process, biomethane and bioethanol fermentation process and comparison of biomethane and bioethanol in terms of yield and energy value is also discussed. These cereal crop residual biomass contribute in the production of renewable and sustainable energy.

### 1. Introduction

In the 21st century, the world economy is highly dependent on various fossil fuels such as crude oil, coal and natural gas for the production of energy, electricity and other goods [1]. Global energy consumption is continuously increasing due to the expansion of human population industrial prosperity, while the fossil fuel reserves are declining. In the current scenario of energy and fuel crisis, there is a need for alternative and renewable sources such as the sun, wind, water, biomass and geothermal heat, to serve this increasing demand for the energy [2,3]. The requirement of electricity may be fulfilled by solar and wind farms while all petroleum-based fuels can be replaced by renewable biomass fuels such as biogas, bioethanol, biodiesel and biohydrogen.

Biomass (food waste, agricultural waste, crop residues, organic fraction of municipal solid waste) is a promising alternative, which can be utilized as the best renewable and sustainable option for meeting the demand and insurance of future energy and fuel supply [137]. In the present scenario, bioenergy contributes 10–15% (approximately 45 EJ) of total world's energy use and numerous studies suggest that the potential market of modern biomass may increase by up to 10–50% by the

year 2050 [4]. Annually, approximately 220 billion tons (on dry weight basis) of renewable biomass is produced worldwide, which is equivalent to 4500 EJ of solar energy captured each year. The energy produced from this biomass may fulfill an annual bioenergy market of 270 EJ [5]. Developing countries like India uses 47% of energy from the renewable biomass [134] and the escalation of energy use in India is 6% annually [136]. Looking at huge energy potential and sustainability, biomass seems to be an attractive substitute to fossil fuels. Optimally, this energy should be produced and utilized without affecting the environment. Direct burning of one ton of dry biomass produces 1599 kg of carbon dioxide, 111.3 kg carbon monoxide, 9.2 kg methane, 5.6 kg hydrocarbon and 4.8 kg particulate matter [6]. Biomass is considered as carbon neutral and direct burning of biomass, theoretically does not contribute to the greenhouse effect, however, for sustainable use, direct burning of biomass is not recommended. Thus, its utilization in the form of fuels and chemical must not affect the environment so that it contributes in protecting the environment with energy generation.

Wood wastes, agriculture crops and their waste byproducts, biogenic waste, municipal solid waste (MSW), waste from processing of food, and aquatic plants and algae are considered as most important

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**Table 1**  
Major cereal crops production in the world in 2014 [51].

Crop	Total cultivated area (million hectares)	Total grain yield (million tons)	Leading Producers
Maize	183.3	920.1	United states, China, Brazil, India, Mexico, Argentina
Wheat	225.4	729.5	European Union, China, India, United states, Russian Federation
Rice (Milled)	161.4	494.4	China, India, Indonesia, Bangladesh, Viet Nam, Thailand

renewable resources for bioenergy production [7,8]. Most of the bioenergy comes from wood and wood waste and its average contribution is 64% of the total bioenergy, while the contribution of MSW, landfill gases, and agricultural residue are 24%, 5% and 5% of total bioenergy, respectively [9–11].

Agricultural residues in the form of agricultural biomass is categorized in a broad category that incorporates the food based portion (oil and simple carbohydrates) of crops (such as corn, sugarcane, beets) and non-food waste (complex carbohydrates) portion (such as leaves, stalks, corn stover, orchard trimmings, rice husk, wheat straw and pearl millet stalk), perennial grasses and biogenic waste. Maize, rice, and wheat are the top three cereal crops grown worldwide and residue produced from these crops is considered to be good substrate for biofuel production [12,13].

Bioethanol production could be an effective way of utilizing lignocellulosic biomass crop residue and wasted crops residues. A whopping amount of bioethanol (491 billion liters) may be produced from 1574 billion kg of dry crop residues and wasted crops per year. This amount is 16 times higher than the actual world bioethanol production [14]. The world bioethanol production increased to 100 million m<sup>3</sup> from 50 million m<sup>3</sup> in just five years from 2007 to 2012. Brazil and the United States fulfill the 80% of the world bioethanol supply, using corn and/or sugarcane as renewable biomass. In the current scenario, non-food raw materials such as sweet sorghum or cassava are becoming the substitute of food-related feedstock. Bioethanol is a developing fuel due to its carbon neutral property, it acts as an octane enhancer in unleaded gasoline; and it is used as oxygenated fuel mix for a cleaner combustion of gasoline, hence reducing tailpipe pollutant emissions and improving the ambient air quality [15,16].

Methane production through anaerobic digestion (AD) is another way to utilize biomass in the form of bioenergy. There are many thermochemical and biological routes of energy generation from biomass in terms of output/input ratio, AD process has maximum value of 28.8 MJ; hence, it is considered to be the most efficient process [17]. According to the report of IPCC 2001, global warming potential of methane over 100 years relative to the carbon dioxide is 23 times higher [18]. Biomethanation process helps in reducing the natural emission of methane caused by self-degradation of organic waste, by utilizing the biomass to produce biomethane in a controlled environment through the AD process. Furthermore, after methane enrichment, biogas can be a good substitute for conventional compressed natural gas (CNG) and can be used for powering the internal combustion engine and for various power generation application [19].

Thus, based on the aforesaid statements, bioconversion of renewable agricultural residue into biofuels such as biomethane and bioethanol is a very effective route for handling the agricultural waste in the form of sustainable bioenergy. This bioenergy potential of biomass may further be enhanced by various pretreatment technologies such as physical, chemical, physicochemical and biological. Pretreatment provides easy accessibility and increased surface area of biomass to the microorganism, which is responsible for biofuel generation from biomass.

In the case of lignocellulosic biomass, it helps to remove lignin and hemicellulose, reduce cellulose crystallinity and make the cellulose easily available for degradation [20]. Among all the pretreatment methods investigated so far, chemical pretreatment has come out to be most promising when followed by AD process [21].

This review presents a comprehensive summary of the waste derived from major renewable cereal crops (maize, wheat, rice), the biofuel potential of the waste by AD and bioethanol fermentation route, and effect of various chemical pretreatment on their biogas potential. It also contains annual production of the generated cereal crop residues, methane and ethanol production potential of these renewable biomass residues, properties of lignocellulosic biomass and the chemical pretreatment method to harness the maximum bioenergy is also discussed.

## 2. Worldwide cereal crop residue and its composition

Agriculture and forestry are two main sources that provide renewable carbon for growing bio-based economy. The vision of bio-based economy is to fulfill the increasing energy and raw material demands of society in a sustainable manner. Agricultural residues may contribute fulfilling this goal as one of the major renewable sources [52]. According to the data of Food and Agriculture Organization (FAO) 2014, maize, wheat and rice are the major cultivated crop all over the world. Table 1 represents the leading producers of these crops, cultivated area under these crops and total grain yield [22].

Hillodhari et al. [22] assessed crop residue biomass and subsequently bioenergy potential of India. They reported that the maximum gross residue and surplus residues come from cereal crops like rice, wheat, and maize. The gross potential is the total amount of residue from a particular crop and surplus residue is the residue left after any competing uses (such as cattle feed, animal bedding, heating and cooking fuel, organic fertilizer). This surplus fraction was considered as a source for bioenergy generation. In India, major crop residue production consist of sugarcane (*Saccharum officinarum*), rice (*Oryza sativa*), wheat (*Triticum aestivum*), maize (*Zea mays*), millet (*Pennisetum glaucum*), cassava (*Manihot esculenta*) and pegion pea (*Cajanus cajan*) ranging from 1950 metric tonnes to 2,76,250 metric tonnes [135]

Table 2a shows bio-power in India and Table 2b shows the generation statistics of maize, wheat and rice in India.

Wheat straw, maize straw, rice straw were considered as three major cereal crops for bioethanol production by Sarkar et al. [23]. These crops provide the residues throughout the year for bioethanol production. Tables 3a, 3b shows the worldwide and Indian scenario for the production of these cereal crops residues. Asia is the major producer of cereal crop residues and a major fraction of these residues comes from rice and wheat straw.

Only a small fraction of total produced residues from these crops is

**Table 2a**  
Year wise cumulative bio-power installed capacity in India [132].

Year	Installed capacity (MW)
2008-09	1751
2009-10	2137
2010-11	2600
2011-12	3095
2012-13	3565
2013-14	4013
2014-15	4165
2015-16	4938
2016-17	8021 <sup>a</sup>

<sup>a</sup> Expected.

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