

Biofuels (Bioethanol, Biodiesel, and Biogas) from Lignocellulosic Biomass :A Review

Rana Abbas Azeez

Petroleum Technology Department, University of Technology - Iraq, Baghdad, Iraq

E-mail:150011@uotechnology.edu.iq

Firas K. Al-Zuhairi

Petroleum Technology Department, University of Technology - Iraq, Baghdad, Iraq

E-mail:150009@uotechnology.edu.iq

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Abstract

Gaseous emissions are from the use of fossil fuels when burned to cause an increase in global warming. Therefore, for sustainable development, consideration should be given to the production of green alternative energies that can be produced from the bio-waste available from food residues, agricultural residues or food factory residues. Converting waste to alternative energies or biofuels is a positive aspect due to the continuous increase in waste that creates environmental problems and traditional methods of waste disposal such as landfills or incineration produce gas. Biofuels production from lignocelluloses materials which are containing carbohydrate polymers and lignin, both of these components considered as a feedstock for produce chemical material, biofuel, biomethane, biohydrogen as alternatives of fossil fuel. In this paper, the researcher reviewed different pretreatments methods and recent technology that can be enhanced degradable of various biowaste or lignocelluloses biomass (agricultural waste, food residue, municipal wastes, and animal waste of) and conversion to biofuel (bioethanol, biodiesel, and biogas). The selection of the pretreatment of cellulosic material depends on the economic cost of producing biofuels; so many researchers around the world were trying to develop alternative energy (biofuel) production technology as an alternative to fossil fuels by reducing the economic cost of biowaste pretreatment.

Keywords: Pretreatments, Biofuel, Lignocellulose Material, Renewable energy.

1. Introduction

The urgent need nowadays is to produce biofuels and rely on alternative energy instead of fossil fuels resulting in air pollution during combustion or refining. Biofuel can be produced from three generations. The first generation is from food, sugar or vegetable oil. This type causes a rise in food prices, increasing deforestation, low water resources it causes negative implications for biodiversity on the planet [1]-[4]. Second-generation for biofuel from biowaste, as well as produce from algae (third generation). Bio-waste is generated from food, agricultural, and municipal waste and it increases daily which leads to an environmental problem as a results emissions of CO₂ and methane from the landfill to atmosphere, about 1.3 billion tons are collected from municipal solid waste around the world and it is expected to increase to 2.2 billion tons by 2025 [5].

Biomass or lignocelluloses material can be used as a low-cost resource for renewable energies production like biofuel and chemicals, but there are limitations of using lignocelluloses as a feedstock for producing biofuel in a large scale. The cost for the selection of pre-treatment methods for biowaste or lignocelluloses materials is the one of most important factor that should be controlled when it is used as the resource for biofuel production, that should be economically and efficient for the breakdown of its complex structure that consists from cellulose, hemicelluloses, lignin and lipids [6]-[11].

The types of used biowaste and different converting technology into biofuels are summarized in Figure (1) [12],[13]. Increase in the marketing value of biofuels production technology from biomass waste, is expected to reach 40 billion by 2023, most marketed countries are Europe and Japan from Asia, America, Brazil, and Australia [14]. It has established factories to produce biofuels from various waste rich in biomass; it has proven that the use of biofuel waste conversion technology is a renewed approach to reducing environmental pollution by not relying entirely on fossil fuels, but this technique needs many handling consideration and depends on a food residues as raw materials varying by locations. Moreover, the efficiency of biological converting technologies are affected mainly by temperature and climate, so no single treatment can be adopted everywhere, besides, the production of biodiesel and bioethanol is expensive because it requires catalyst and solvent extraction [15].

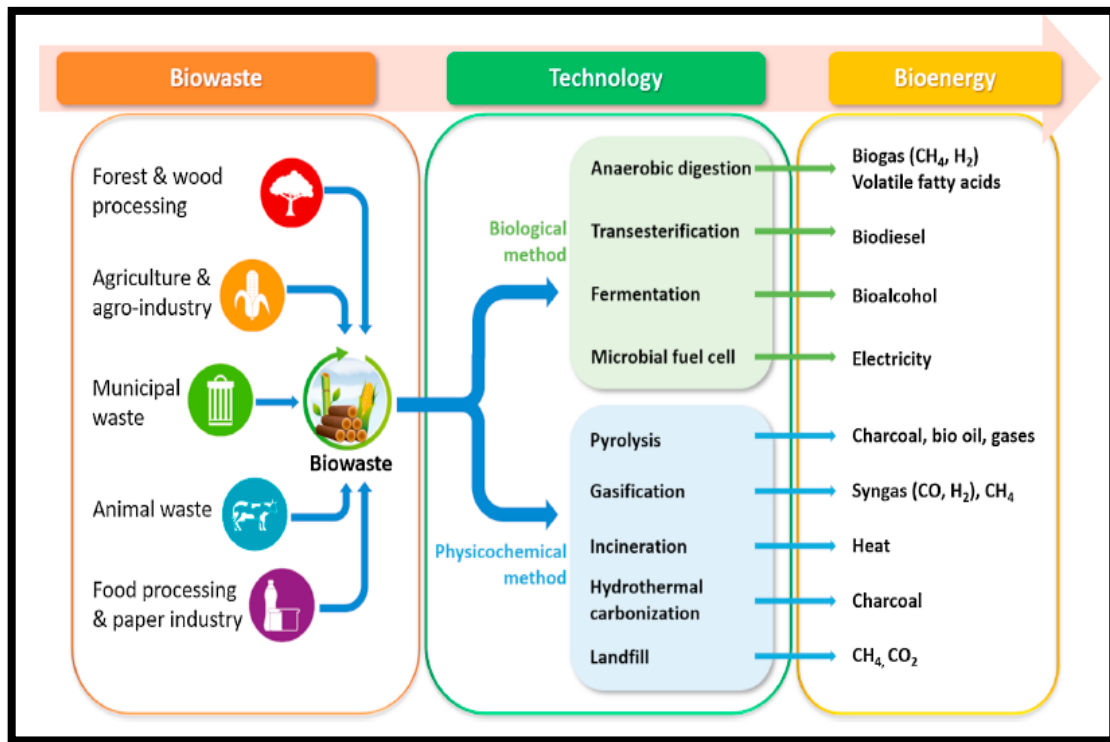


Figure 1. Scheme showing the production of biofuels from various bio-waste [13].

1.2. Lignocellulosic Biomass

Lignocellulose consists of cellulose, hemicellulose, lignin, pectins, proteins, and other inorganic materials [16], the composition of the different substrate of lignocelluloses materials and its structure are listed in the Table (1), and Figure(2) [17].

Cellulose is a linear chain of hundreds to 10 thousand of D- glucose molecules bound together by glycosidic bonds, lignocelluloses biomass composed of crystalline and amorphous forms of cellulose, parallel bundles are surrounded by cellulose chains by strong hydrogen bonding between crystalline forms [18]. Hemicellulose is the second most abundant natural carbohydrate polymer on earth, a complex structure of the carbohydrate, encompasses xylan, xyloglucan. Hemicelluloses with branched structure, amorphous, and resistance to hydrolysis are weak but decomposes with acids into small molecules [19]. Lignin, is the third bio-polymer found in nature, composed of phenyl propane (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) unit linked with ester bonds that form a complex structure with hemicellulose to encapsulate [20],[21]. This enables it to resist hydrolysis and enzymes and its biological function is to protect the cell wall. Biomass-rich lignin is more resistant to the degradation of hemicellulose cellulose and converted to glucose, In addition, during the decomposition it may be accompanied by the formation of furan compound that can cause inhibition in the process of fermentation or digestion [22].

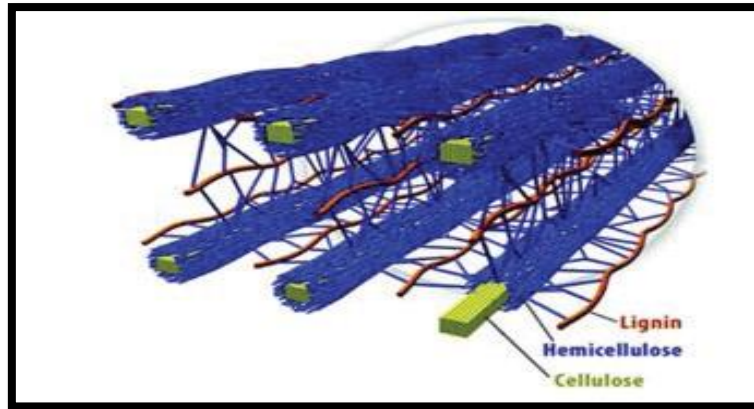


Figure2. Structure of lignocelluloses biomass [17].

Table 1. The composition of various lignocelluloses biomass.

Substrate	Cellulose%	Hemicellulose%	Lignin%	Reference
Corn stover	37.5	30	10.3	Li X et.al.,2010[23]
Sugarcane bagasse	45	20	30	Stanmore,(2010)[24], Samaraha and Khakifirooz (2011)[25]
Sugar beet waste	38.6	26.5	12.1	Al-Hilo et.al., (2007) [26]
Rice straw	38.3	21.3	12.5	Dai et al., (2017)[27]
Rice husk	34.4	29.3	19.2	Mahvi, (2004) [28]
Wheat straw	37.5-40	21-26	11-2.9	Khan and Mubeen ,(2012) [29]
Oat straw	39.4	27.1	20.7	Chandra, (2012) [30]
Corn cobs	38.8±2.5	44.4±5.2	11.9±2.3	Pointner, (2014) [31]
Banana waste	60.25–65.21	48.20–59.2	5.55–10.35	Gonzale et. al., (2012) [32]
Pineapple	70.55–82.31	18.73–21.90	5.35–12.33	Reddy and Yan (2005) [33]
Coconut (coir)	36.62–43.21	0.15–0.25	41.23–45.33	Satyanarayana et. al., (2009) [34]
Nut shells	25-30	25-30	30–40	Chandra et.al., (2012) [30]
Sweet sorghum	45	27	21	Kim and Day (2011) 35
Hazelnut Shells	16.67	13.30	51.30	Hoşgün and Bozan (2019)[36]

2. Treatment of Lignocelluloses Biomass

Biowaste (lignocelluloses material) cannot be used directly as a feedstock for production biofuels without any pre-treatment due to their complex structure. Therefore hydrolysis lignocelluloses biomass to intermediates components; this leads to the economic ineffectiveness of biomass-based technology marketing [37],[38]. In general, physical, chemical, and biological are the major pretreatment approaches and it depends exclusively on the application, the combining between two or more pretreatment techniques such as physicochemical which is preferred for reducing the number of followed operational process and minimizing of the undesirable production, as shown in Figure (3) [30].

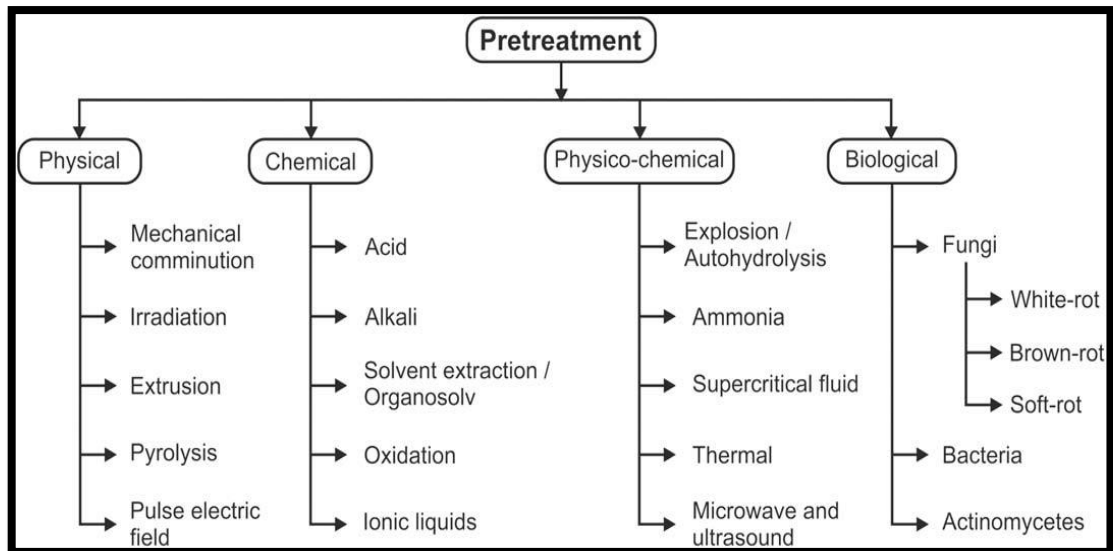


Figure 3. Scheme for various pretreatment of biomass[30].

2.1. Pretreatment of Lignocelluloses Material to Biofuel

Conversion of biomass rich by lignocelluloses such as agricultural waste, cane, sugar beet wastes, and wood to liquid biofuels, that represents an environmentally friendly fuel to reduce the emission of greenhouse gases, the most commonly methods used for pretreatment of organic wastes are grinding and cutting which classified as primary physical treatment[39],[40].

The alkaline, acidic, ozonolysis, oxidative, and ionic liquids were classified as a chemical pretreatment process, also many studies focus on increasing the degradation of complex structure of lignocelluloses biomass at hydrolysis step by combined of thermal treatments with pressure was also used to increase the solubility of carbohydrates called hydrothermal or thermobaric method[41], on the other hand, the previous studies were found the acid treatment with high-temperature is the best way to the degradation of lignocelluloses biomass [42]-[44].

Chiranjeevi et al., (2018) presented the higher quantity of mono sugar obtained from rice straw after treatment with acids was about 4.2 times than of untreated by treated of rice straw with 1% (w/v) boric acid with 0.75 % (v/v) of H₂SO₄ and (0.5 % v/v) of glycerol for 20 min at 150°C [45].

3. Liquid Biofuel from Lignocelluloses Biomass

In recent decades, there has been considerable interest in the production of liquid biofuels bioethanol and biodiesel as alternatives to traditional fuels to decrease the negative effects on the environment [46].

3.1. Bioethanol

Bioethanol can be produced from the fermentation of sugar or lignocellulose materials after conversion to mono or disaccharide, many forms of sugar can be extracted from plants by different pretreatment such as thermal treatment, chemical treatment, and irradiation process [47]. In the economic point of view uses of lignocellulosic residues from plant or food products as feedstock's having more advantages by compared with sugar or starch, the high quantity of sugar or starch in corn and sugarcane can be easily fermented to bioethanol [48].

Otherwise the conversion lignocellulose material to biofuel required more pre-treatment before digested because the pretreatment methods have a significant impact on the effective production of ethanol from biomass, however, intensive research is still necessary to develop new and more efficient treatment processes for converting lignocellulose biomass into ethanol [49].

Many attempt were done to distinguish the effect of various pretreatment methods on hydrolysis of lignocelluloses materials. Al-Hilo et al., (2007) presenting the production of bioethanol from sugar beet waste which was increased after pretreatment biomass with 0.25M NaOH that increase the ability of lignocelluloses material to hydrolysis with (2N H₂SO₄) to mono sugar[26]. Rajput and Visvanathan(2018) reported the heat pretreatment of wheat straw at 180 ° C increase biofuel production

by 53% when compared with untreated one in anaerobic digestion[50]. Bona et al., (2018) reported the production of bioethanol were increased by the treatment of lignocelluloses in a feed stocks with 3.5% H₂SO₄ at 121 °C for 30 min, followed by enzymatic hydrolysis, as a result, it increases the amount of sugar from cattle, matter pig and poultry manure were about 230.16, 160.40 and 98.40 mg g⁻¹ dry matter respectively [51].

3.2. Biodiesel

Biodiesel is one of the most important environmental friendly fuel which can be produced from different types of biomass, that can be used alone or blended with petrodiesel to reduce gas emissions and other impurities during combustion as results enhancing of its physical properties such as cetane number, flash point, specific gravity and sulfur content where about 58, 110 oC, 0.87 and ≈ 0.0 respectively by comparison with petrodiesel where about 53, 70 oC, 0.85 and ≤ 1 [52]-[54].

Biodiesel was produced by transesterification and esterification of vegetable or animal oils, in this process, the triglycerides are converted to diglycerides, to generate monoglycerides, then the monoglycerides through reacting with alcohols convert into esters (biodiesel) and glycerol. The transesterification reaction occurs in the presence of different types of catalysts like, acid catalyst, enzyme catalyst, base catalyst (KOH, NaOH) [55], as shown in Figure (4)[56],[57].

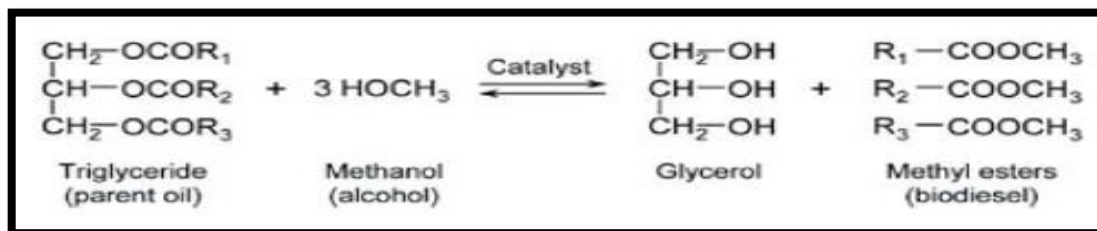


Figure 4. Transesterification process to produce biodiesel

There are two stages for the production of biodiesel from biowaste, the first one is lipids extraction that can be done by mechanical, chemical, and enzymatic methods. In the last stage the extracted lipids esterified with alcohols [58],[59]. Pastore et al.,(2013) extracted the lipids from dewatered sludge (total SS: 15 wt.%) in the first step by hexane and followed to the second step esterification using methanol in the presence of acid catalyst (H₂SO₄)[60]. Ananthi et al.,(2019) investigated amount of lipid was about 37.99 % were obtained from treated of lignocelluloses material (sugar cane bagasse) by the steam explosion at 121 °C for two hours, lipid content considered one of the most important feedstock in biodiesel production [61].

Recently, several attempts have been done to produce biodiesel from microalgae which are called 3rd generation biofuel. The microalgae cells utilized CO₂ and organic carbon to produce lipids, that is varied from species to others [62], which are classified for five types, Brown, Red, Blue-green, Green, and Yellow-green algae depends on pigmentation [63]. The production of biodiesel from algae is inexpensive, and this process is carried out through the following steps: (i) algae cultivation (ii) harvesting, (iii) drying and processing, and finally the trans-esterification step [64],[65].

Various investigations were conducted to extract oil from algae, Kim et al., (2012) extracted lipids from commercial and cultivated microalgae (*Chlorella Vulgaris*) by Bligh and Dyer's technique, they obtained 10.6% and 11.1%, respectively, while 12.5% 19.0% lipids content when treated with ionic liquid [CF₃SO₃] with methanol [66].

Hossain and Salleh (2008) concluded higher amount of algal oil and biodiesel can be produced from *Oedogonium* than *Spirogyra* sp.[67]. Gouveia and Oliveira (2009) investigated various microalgae in order to select the best species for synthesis biodiesel. They found that the *Neochloris oleabundans* from freshwater and *Nannochloropsis* sp. from marine are best algae for biodiesel production which is attributed to the lipids content that are 29.0% and 28.7%, respectively [68].

3.3. Biogas from Lignocellulosic

Anaerobic digestion (AD) process is a biological technique for the biodegradation of biomass by microorganisms in the absence of oxygen. This technique used different types of biomass in feedstock such as agriculture, animals and municipal solid wastes to produce biogas which consists a mixture of gases such as methane, carbon dioxide, and small amounts of other gases [69]-[72]. AD technique

involves several steps, which are hydrolysis, acidogenesis, acetogenesis, and methanogenesis by a group of microorganisms shown, in Figure (5). During hydrolysis microbial step the complex structure of biomass is converted to simple molecules [73], these components are digested by acidogenic bacteria into different volatile fatty acids (VFAs), hydrogen and carbon dioxide, that reduced to acetic acid by acetogenic bacteria, in the last step. The intermediate products converted to methane, carbon dioxide and water under effect of methanogenic bacteria [74].

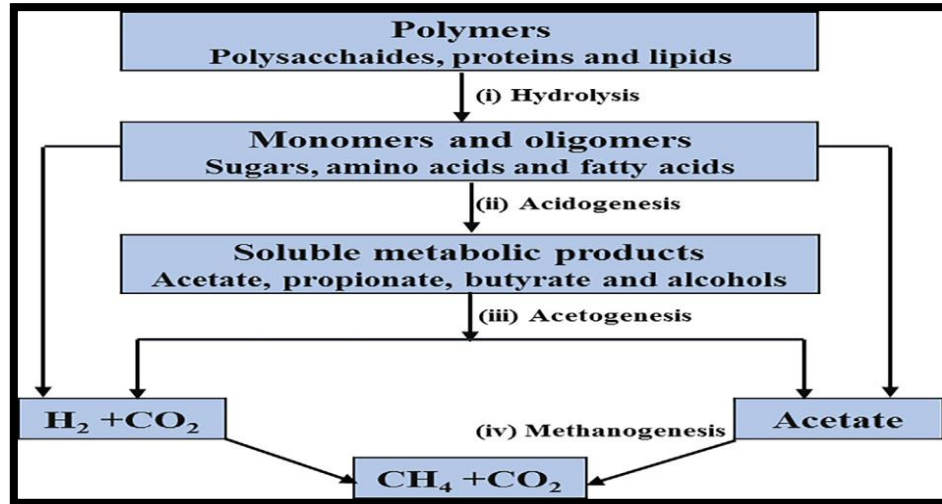


Figure 5. Anaerobic digestion for production biogas[73].

Anaerobic digestion can be enhanced toward increase biogas production by choosing the best pretreatment techniques for biomass in feedstock's, trace metal additive and process conditions, temperature, pH, C/N, total solid or volatile solid percentage and operation mode batch or continuous are most important conditions should be controlled during digestion period[75, 76]. Choi et al. (2018) presented the thermal pretreatment for activated sludge at 180 °C for 76 min increases the biodegradation of lignocelluloses materials while led to increases the desired product by 17 % when compared with untreated biomass [77]. Costa et al., (2014) reported the anaerobic biodegradables of sugar cane bagasse were enhanced toward sugar degradable and biomethane production by thermochemical pretreatment for feedstocks [78]. Cesaro et al., (2014) founded when pretreatment of biomass with ultrasonic inputs in the range 31-93 W h/L was improved biogas production to 71%. from organic substrates, which attributed to increasing solubility of cellulose and hemicelluloses[79]. Zeynali et.al.(2017) studied the effect of ultrasonic pretreatment for improved biogas production from fruit and vegetable waste with different treatment period 9, 18 and 27 min at 20 kHz., they founded the highest yield of biomethane was produced at 18 min [80].

Oxidative with hydrogen peroxide (H₂O₂) was considered another pretreatment method for the breakdown of the complex structure of biomass, which has the ability to increase the cellulose percentage by delignification from lignocelluloses materials [81].

Venturin et al. (2018) presented the combined alkaline pretreatment with H₂O₂ for corn stem increases the biogas production by 22% increase [82]. Song et al. (2013) demonstrated an increase in biogas production by 88% when pretreatment with H₂O₂ [83]. Michalska et al. (2012) founded that good results can be obtained when the oxidation and biological methods were combined in the pretreatment step [84].

Food waste is considered one of the most vital wastes available and higher ability to biodegradable towards biogas production that can be obtained from the food of homes, bakery, and dairy products and food processing plants. It was observed in the last two decades the amount of food waste has been increased in Asian countries from 278 to 416 million tons during 2005 to 2025; this is due to the increased population growth [85, 86].

Zamanzadeh et al., (2017) produced biogas from co-digestion of food waste and cow manure at mesophilic condition. The best yield of biogas was about 480 mL/g VS with food waste alone in a feedstock's and it was increased by 26% when co-digestion with cow manures [87].

4. Applications of Nanomaterials in Biofuel

In recent years, nanomaterial additives were considered the advanced way that were used to enhance the efficiency of biofuels production from biomass [88], which improved the cellulase enzyme performance and enhanced biodegradable of lignocelluloses of biomass [89]. Figure (6) illustrated different applications of nanomaterial in biofuel production [90].

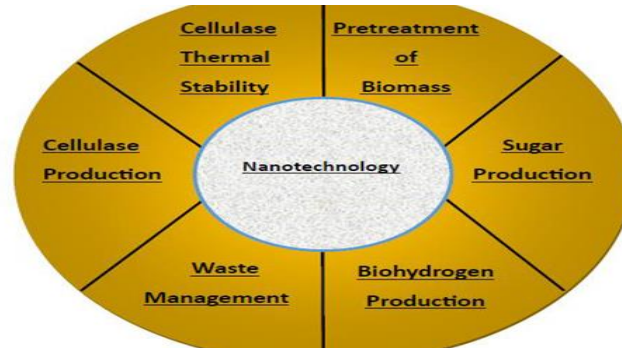


Figure6. A diagram illustrating the applications of nanoparticles in biofuel production [90].

Many studies have been focused on improving the efficiency of lignocelluloses material bioconversion to biofuel using various types of nanomaterial. In one of the studies by Wei et al. (2015) they observed the production of sugar from corn stoves at hydrolyzes step was increased when iron oxide nanoparticle was used as additive to enhance the acid pretreatment method due to an increase of glucose and cellulose percentage by 13-19 % when compared to acid-treated alone [91]. Another study by Yang et al. (2015) reported the bioconversion of lignocellulose material to biofuel was improved in the presence of reduced graphene oxide functionalized with Fe₃O₄ nanoparticles [92].

The benefits of using nanoparticles in the biodiesel process, improves hydrocarbon combustion and reduces nitrogen oxide [93]. Hu et al., (2011) founded the biodiesel yield more than 95% when nano KF/CaO-FeO was added into transesterification process [94].

The addition of a several types of nanoparticles into anaerobic digestion (AD) improved the activity of microorganisms by increasing the movement of electrons in the digestion process as well as improving the kinetics of bio-hydrogen production which leads to increasing the production yield [95],[96]. García et al.,(2013) founded the addition of 1120 mg/l from nano TiO₂ to AD increases biogas yield by 10% [97], Abdelsalam et al.,(2016) presented the production of biogas and biomethane increased by 73% and 115.66% respectively when 20 mg/L from nano Fe₃O₄ was added to fresh raw at 37oC [98].

5. Conclusion

In this review, the pretreatment methods for lignocellulose biomass that has been used as feedstock for the production of liquid and gases biofuel that considers the alternative source of energy instead of traditional fossil fuels as well as satisfies the decreases of needed energy and assist of environmental protection. The lower cost and local availability of biomass makes it's a major contender to be used as raw material for the production of different types of biofuel.

Moreover, the recent technology is used to enhance the efficiency of biofuels production from biomass was also reviewed which is a nanomaterial additive. This technology needed a lot of effort and research to reduce the economic cost of produced biofuel by comparison with added nanomaterial and chosen pretreatment method.

Conflicts of Interest

The author declares that they have no conflicts of interest.

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الوقود الحيوي (بايوإيثانول، بايوديزل، الغاز الحيوي) من الكتلة الحيوية اللجينية الخلوية: مراجعة

رنا عباس عزيز

قسم تكنولوجيا النفط، الجامعة التكنولوجية، بغداد، العراق

E-mail:150011@uotechnology.edu.iq

فراس خليل الزهيري

قسم تكنولوجيا النفط، الجامعة التكنولوجية، بغداد، العراق

E-mail:150009@uotechnology.edu.iq

الخلاصة

الانبعاثات الغازية الناتجة عن استخدام الوقود الأحفوري عند حرقها تسبب زيادة في الاحتباس الحراري. لذلك، من أجل التنمية المستدامة، ينبغي إيلاء الاعتبار لإنتاج طاقات بديلة خضراء يمكن إنتاجها من المخلفات الحيوية المتاحة من مخلفات الطعام أو المخلفات الزراعية أو مخلفات مصانع الأغذية. يعد تحويل النفايات إلى طاقات بديلة أو وقود حيوي جانباً إيجابياً نظراً للزيادة المستمرة في النفايات التي تخلق مشاكل بيئية. إن الأساليب التقليدية للتخلص من النفايات مثل مدافن النفايات أو الحرق تنتج غازات الاحتباس الحراري.

إنتاج الوقود الحيوي من مواد اللجينية الخلوية التي تحتوي على بوليمرات الكربوهيدرات واللجنين المكونين للذان يعتبران بمثابة وسيط لإنتاج المواد الكيميائية والوقود الحيوي والبيوميثان وهيدروجين حيوي كبديل للوقود الأحفوري. في هذا المقال، قمنا بمراجعة طرق المعالجة المختلفة والتقنية الحديثة التي يمكن لها أن تحسن التحلل للكتلة الحيوية السليلوزية المختلفة (النفايات الزراعية، مخلفات الطعام، النفايات البلدية، ومخلفات الحيوانات في) وتحويلها إلى وقود حيوي (الإيثانول، الديزل الحيوي، الغاز الحيوي). يتم اعتماد اختيار المعالجة المسبقة للمواد السليلوزية على التكلفة الاقتصادية لإنتاج الوقود الحيوي، وقد أجريت العديد من الدراسات في جميع أنحاء العالم من أجل تطوير تكنولوجيا إنتاج الطاقة البديلة (الوقود الحيوي) كبديل للوقود الأحفوري عن طريق تقليل التكلفة الاقتصادية لمعالجة النفايات البيولوجية.

الكلمات الدالة: المعالجة الأولية، الوقود الحيوي، المادة اللجينية الخلوية، الطاقات المتجددة.