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Biomass to Biofuels: Conversion Processes and Challenges in Second-generation Technologies

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Abstract—This paper illustrates the latest advancements in the opportunity of using biomass as an alternative source of energy to produce biofuel products. The high demand on fossil fuels should be embraced by studying available biomass feedstocks such as starch and lignocellulosic. This study shows that every feedstock can produce a unique biofuel type. In fact, lignocellulosic is the core material to produce biofuels from non-food biomass sources, known as the second-generation, where this route is more efficient and environmental friendly. However, gasification and pyrolysis are the most common techniques to convert biomass into chemicals. Thus, the characteristics of various reactors have been discussed to show that the reactor selection depends on the desired product as well as the feedstock state. Ethyl tertiary butyl ether (ETBE) and Fatty acid methyl esters (FAMEs) are the prime biofuel products from biomass. Moreover, more evaluations and studies were performed regarding the oxygen feedstock and large-scale of second-generation issues. It is possible to remove oxygen totally or partially to increase the total amount of produced energy, but this may result in the formation of charcoal or hydrogen.

Index Terms— Biomass, Biofuels, Gasification, Pyrolysis, Second-generation, Oxygen, Large-scale, Energy, Environment, Lignocellulosic.

1 Introduction

Principally, crude oil is the main source of energy to nations around the world. However, the increasing demand on transportation fuels will lead to more greenhouse gases and enormous consumption of the finite crude oil supply. Accordingly, alternative energy sources such as biomass is very optimal for transport purposes. Biomass processes contributed in the production of hydrogen, as a side product, which is also broadly known as a major source of energy. Further, there are other products that come from the biomass conversion called biofuels blends such as ethanol and fatty acid methyl esters (FAMEs) which can be added to either gasoline or diesel fuels respectively without any required modifications to the engine design.

According to Taylor, in mid-2008, the rose in the food prices resulted in having poor energy balances for biomass technologies. However, alternative energy sources for fossil fuels have to be in the industry before facing a huge problem with the increasing transportation fuel demand. Bioethanol and biodiesel are the most common fuels that can be produced from different biomass processes. In fact, Biorefining is very similar to many refining processes used in petroleum refineries, except that the core feedstock in biorefining is biomass rather than hydrocarbon liquids. Nowadays, high population growth increased the demand on energy vastly. The problem is that the majority of our energy comes from fossil fuels. It is estimated that there will be an increase of 32 million barrels in the total worldwide oil demand by 2030. Therefore, the concept of this review is to discuss the development and the challenges of the second-generation biomass technologies by understanding various feedstocks, reducing the oxygen content and evaluating the large-scale issue.

2 Biomass

Biomass is a renewable energy source that is environmental friendly. Biomass technologies are able to overcome crucial issues such as climate change, energy security and rural development. This paper illustrates the current biomass status in the industry and the common existing biomass feedstocks.

The biomass main components are resulted from the reaction between carbon dioxide, water and sunlight as energy source. Cellulose, hemi-cellulose and lignin are the three major components of biomass material with other organic and inorganic elements. It is easy to elucidate this by stating that cellulose is a polymer of glucose while hemi-cellulose is an oligomer that consists of C6 and C5 structure. Previous studies verified that the energy quantity of such an amount of sugar or starch usually increases with lower oxygen presence in one of the three building blocks.

3 Biomass Feedstocks

There are three different classes of biomass feedstocks: starchy, triglyceride and lignocellulosic. Each one has it is own characteristics; for example, starchy biomass consists of glucose which is easy to process to bioethanol. On the other hand, triglyceride feedstocks are fatty acids and glycerol that are used in the production of biodiesel while lignocellulosic biomass always presents in agriculture residues, wood and mu-

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nicipal wastes in large quantities. The first-generation biomass feedstock comes from food sources where the second-generation is extracted from non-food sources. Lignocellulosic is considered in the second-generation biomass feedstock group. As a result of previous details, Biomass feedstocks can be divided into three unique categories.

3.1 Carbohydrates and Lignin

Carbohydrates are the most common biomass feedstock. Starch and varieties of sugars like glucose, galactose and 5-carbon sugars are all examples of carbohydrates which are used to produce ethanol. On the other hand, lignocellulosic biomass consists of cellulose, hemicellulose and lignin that contains C5 – C6 sugars which are provided in crops or residues.

3.2 Triglycerides

Fatty acids feedstocks with larger carbon chain length ranging between C8 and C20. Typically, glycerine is the main component in oils and fats which can be extracted from various vegetable and animal raw materials. Biodiesel is the most common product that is processed from this feedstock.

3.3 Mixed Organic Residues

Municipal Solid Waste (MSW), industrial wastes and wild residues are other biomass feedstock sources. The high moisture content (70%) of these feedstocks make them ideally for the production of biogas by anaerobic digestion process.

4 Lignocellulosic biomass

In practice, lignocellulosic biomass must be broken into parts to be processed efficiently. Then, isolation of the biomass is required and this isolation can be achieved through pretreatment and pyrolysis processes. Lignocellulosic biomass contains about 50% cellulose, 20% lignin and 30% hemicellulose.

4.1 Lignin

It provides the plant with rigidity and ability to transport water and solutes. This type of biomass can be removed to isolate the carbohydrate by depolymerization/solubilization in alkaline-alcohol solutions. It is mainly used for the production of biooils and aromatics.

4.2 Hemicellulose

This is preferable to be extracted by physical or chemical extraction and hydrolysis methods in order to recover glucose from cellulose easily. Xylose monomers yield in this process which is used for ethanol production.

4.3 Cellulose

It is normally isolated within the two other previous elements which makes it harder to isolate glucose monomers of cellulose before pretreatment of lignin and lignocellulose.

5 Biofuels Types

5.1 First-generation Biofuels

This type includes conventional technologies are able to produce different biofuels from food sources like sugar, vegetable oil, fats and starch. The most common biofuels in this category are bioethanol, biodiesel and biogas. These products are mainly used as transportation fuels while biogas can also be utilized for electricity generation. Easy conversion process and high sugar or oil concentration are the advantages of the first generation path. However, there are some ethical impacts due to the utilization of large food quantities for oil production instead of producing food which make it difficult to go for this approach.

5.2 Second-generation Biofuels

This is the potential choice where non-conventional technologies are capable to produce various biofuels from non-food crops like agricultural and forestry residues. Lignocellulose is the core material in this route. This way of production will allow us to have more efficient biofuels as well as improved environmental performance. Today, there is a huge amount of non-food lignocellulosic biomass feedstock in farms and agriculture residues or Municipal Solid Wastes (MSW). This process is still under research and it could be introduced to the market within 10 years.

6 Biomass Conversion Processes

Bioethanol and biodiesel are the most famous products out of biofuel production since they can be utilized in gasoline or diesel engines without any modifications. The processing method is very connected to the order of different chemical processes that we need to carry out such as doing a pretreatment process before the hydrolysis process of bioethanol from sugar.

The conversion of cellulosic biomass often occurred by thermal reactions which are usually carried in the presence of a catalyst in order to have a wide range of fuel hydrocarbons. Sometimes biomass goes through fractionation/ hydrolysis processes by biological or chemical ways.

1. **Gasification:** it is the production of syngas through partial combustion, 1000 K
2. **Pyrolysis:** biomass is converted by thermal anaerobic decomposition, 700 K
3. **Liquefaction:** catalytic thermal conversion of large biomass molecules, 625 K
4. **Hydrolysis:** ideal for lignocellulose utilization for the purpose of high selectivity

The most common conversion techniques in the biomass industry are gasification and pyrolysis. The definition of both ways with their different reactor types are investigated below.

6.1 Gasification

Gasification is the conversion of biomass into syngas at high temperatures with a partial oxidation rate. The produced syngas can be utilized for heat generation or to produce liquid transportation fuels. It is important to have the syngas product free of nitrogen gas in order to be suitable in further processes to have liquid fuels. The gasification agent play a key role in controlling the syngas heating value; for example, although that steam and oxygen agents are costly, they are capable to increase the H2/CO ratio which consequently elevates the heating value of the syngas. The commercial gasification types are fluidized and fixed-bed reactors. Still, there are other reactor types in the industry.

1. **Fluidized-bed gasification:** a gasifying suspension will transfer particles into liquids. The advantages of this choice is that there will be a uniform temperature distribution with higher contact between solid and gas allowing us to gasify different biomass feedstocks.
2. **Dual fluidized bed gasification:** the gasification occurs in a first reactor where the combustion is done in a second one. Steam is the gasify agent which is able to produce high hydrogen content products (40%). The hydrogen products are ideal for a chemical synthesis.
3. **Fixed bed gasification:** the raw material is fixed while the gas is passing through it. The flowing gas is possible in different directions: updraft, downdraft or cross flow. The benefits of this selection are the high mixing and the larger reaction rates.
4. **Supercritical water gasification:** biomass conversion by the use of water flow that may reach up to 80% of the total feed percentage. This process improves reactions performance without the need to an expensive drying step.
5. **Plasma gasification:** the use of electrical currents to strip electrons from gas molecules. It operates at very high temperatures from 2000 to 30000ºC.

6.2 Pyrolysis

The conversion of biomass materials into syngas at 1000ºC without the presence of oxygen is called thermal treatment or pyrolysis. The most vital factor in this process is the temperature. In other words, the manipulation in the process temperature will allow us to choose any product type that we need either gas, solid or liquid. There are different types of pyrolysis process.

1. **Slow pyrolysis:** operated at low temperature and slow reaction rates. The process is applicable in both fixed bed and tubular reactors.
2. **Fast pyrolysis:** the biomass is processed quickly at elevated temperatures in the absence of oxygen. It is used to produce high-grade biooils. This process is successful in many kinds of reactors.
3. **Flash pyrolysis:** this process is characterized by having only several seconds for the reaction time at a very high heating rate. The major issue for flash processes is that the high ash content could reduce the product quality and stability.
4. **Catalytic biomass pyrolysis:** the liquid oil that is obtained from the three previous pyrolysis techniques has to be upgraded into transportation fuels by the removal of both oxygen and water through catalytic pyrolysis.

7 Biofuel Products

There are many biomass fuel blends which can increase fuels efficiency dramatically. In case of gasoline, sugar crops can be processed through fermentation techniques in order to have ethyl tertiary butyl ether (ETBE). ETBE is preferred over methyl tertiary butyl ether (MTBE), which produced from oil, since ETBE is an environmental friendly anti-knocking chemical in gasoline engines. Levulinic acid is another chemical that comes from lignocellulose to methyltetrahydrofuran (MTHF) which can be blended with gasoline. In addition, methyl and ethyl are other blends for diesel. Also, γ-valerolactone (GVL) from levulinic acid in aqueous media undergoes two reactions, catalytic and oligomerization, on a dual reactor in order to have liquid hydrocarbon fuels like butane.

Fatty acid methyl esters (FAMEs) is an alternative fuel for 1-methylnaphtalene. FAMEs can be obtained from vegetable oils or fats by a trans-esterification process with methanol. This product will allow us to replace other toxic lubricating agents in diesel engines that contains sulfur compounds. Another product is called Furfural and hydroxymehylfurfural (HMF). HMF is usually produced from cellulose fractions to the production of linear alkanes such as diesel or jet fuel. Aldol condensation is applied to form larger hydrocarbons C9 to C15.

8 Challenges and Suggestions

8.1 Oxygen Issue in Biomass Feedstocks

In the conversion of lignocellulosic biomass to liquid fuels, our concern is the removal of oxygen during the formation of carbon bonds in order to control the final molecular weight of the product. The more oxygen we have, the less energy we can produce from that material. However, the catalytic upgrading in the chemical system will allow us to remove oxygen totally. When we look at the outlook between fossil fuels and biofuels products, we will notice that the presence of oxygen in biofuels lowers the total energy. Thus, various chemical techniques were studied to eliminate oxygen and to have higher energy.

1. **Removal of all oxygen from carbohydrate-rich biomass and upgrading to higher alkanes:** total removal of oxygen can be carried through three different reactions. Each one will produce either carbon dioxide, water or syngas. Rich hydrogen products are resulted from carbon dioxide way. Charcoal will be the final

product in case of going through water route. The last path, syngas, will lead to a co-formation of hydrogen.

2. **Partial elimination of oxygen from carbohydrates as CO2 or H2O:** the elimination of less amounts of carbon dioxide and water should upgrade biofuels to have much energy. Products like ethanol and dimethyl either are treated by partial elimination process. Ethanol is usually the main product from sugar fermentation with carbon dioxide as a side product. Dimethyl either is another product with the same gross formula. More elimination of water will result in the formation of charcoal with loss of all undesired oxygen.
3. **Applicability of partially deoxygenized biomass products in transport fuels:** small chain length, unsaturated hydrocarbons and cyclic structure of biofuels are the major obstacles for having higher energy from biofuels. The two previous methods have the ability to reduce oxygen substantially to increase the amount of energy per unit mass of biofuels. Product stability can be achieved through etherification, esterification and adolisation processes where the unsaturation problem can be solved by hydrogenation and cyclisation.

8.2 Large-scale of Second-generation Technologies

First generation process is mainly used to produce biofuels and biodiesel from food crops. However, second and third generation processes are more advanced while the utilization of lignocellulose and algae becomes accessible. Still, large-scale applications of the advanced technologies are not approved.

Therefore, there are three key scientific advances necessary for a second-generation biorefinery to work. First, better use of feedstock is a key scientific challenge in which scientists should develop more efficient and cost-effective hydrolysis and fermentation processes at large-scale. Secondly, new feedstock design processes have to be established to enhance the required plant breakdown through several biological processes. Finally, better technology to model and asses the breakdown of lignocellulose processes is another necessity to construct biorefinery plants without hesitations.

9 Conclusion

The high growth in demand for energy should lead us to develop the second-generation biomass technologies in order to cover future transport fuels demand. The key advantage of utilizing biomass is that we can reduce the demand on fossil fuels. Biomass is a secure energy supply that will not diminish as long as plants and animals are available. Studies showed that biorefinery alternative would allow us to deal with the climate change problem because biomass technologies reduce carbon dioxide emissions. The potential of biomass technologies is in possibilities of processing un-food feedstocks with higher sustainability.

The easiest way to convert biomass into more beneficial products through syngas. Oxygen elimination and higher hydrocarbon chains are the main obstacles in the biomass industry. There are various recent thermochemical technologies for the transformation of biomass into useful products. In gasification zone, the most common interesting technologies are fluidized-bed reactors and downstream edge. On the other hand, the most used pyrolysis technology is the catalytic process in which there is a possibility to obtain transportation fuels by using different catalysts. In closing, considerations of pilot plants regarding the second-generation technologies and more details about the behavior of biomass feedstocks inside different reactors should be investigated more to avoid any unexpected outcomes and to have feasible large-scale biomass plants.

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