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A Review of Major Pre-treatment Strategies for Producing Fuel Ethanol using Cellulosic Crop Biomass and Forest Residues as Feedstock

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ABSTRACT: The energy crisis, increasing concern about global climate change and other environmental challenges relating to energy/power production have ensured rapid development in the production of biofuels (especially bioethanol) as substitute to the conventional liquid transportation fuels. Over the last two decades, bioethanol has received significant attention and current acceptable pathway involves the conversion of non-food starch-rich materials (lignocellulosic materials) to ethanol and other value-add products. Essentially, these four major steps suffice for modern production of cellulosic ethanol: - pre-treatment and hydrolysis of biomass, fermentation of sugar complexes to ethanol, lignin recovery and ethanol refining. However, pre-treatment process is critical due to it cutting-edge within the entire value chain mostly on the yield of fermentable sugars from the feedstock. This review highlights several techniques put forward to improve biomass pre-treatment based on recent trend in literature. Based on the analysis of these methods, a sustainable bioprocess pathway was recommended to utilize a mix-feed of oil palm and sawmill residues for ethanol production.

KEYWORDS: lignocellulosic biomass, pre-treatment, bioethanol, sustainable bioprocess

I. INTRODUCTION

Problems relating to climate change and environmental concerns are perhaps the greatest challenge confronting humans and nature at the moment (UNEP, 2016). Many scientific theories have been propounded by researchers to be the root-cause (Uhl, 2016; Rosenzweig et al., 2008; Meehl et al., 2000) and at the crux of this problem lies the unsustainable manner at which energy resources are being deployed for usage (Ite et al., 2013). This understanding provides much motivation for biofuels development as substitute and alternatives to the conventional liquid transportation fuels.

Over the two decades, developments around the biofuels industry has surpassed the projection of experts within this research domain. This is unconnected to the increasing pressure on the urgent need to cut down on greenhouse gas emissions. The development has been further strengthened by the fact that mixture contained in most biofuels (especially bioethanol) are less toxic and has less carbon footprint when compared with fossil fuels (Ohgren et al., 2007). For instance, studies have shown that liquid fuels containing ethanol has higher octane number which according to studies reduces need for toxic, octane-enhancing supplements like methyl butyl ether (Lynd et al., 1991; Sheehan et al., 2003). In a related development, He et al., (2008) showed that the total emission of carbon monoxide and non-combusted hydrocarbons are reduced to a great extent in fuels containing ethanol. This they attributed to the presence of oxygen in ethanol molecules. Other study by Galbe et al., (2002) resolved that ethanol has the capacity to provide energy that is sufficient to drive between 75% to 80% of a particular distance as the same amount of gasoline. These probably explain why bioethanol has remained the dominant and most patronised liquid transportation biofuel in the world.

Presently across the world, commercial and large scale production of bioethanol is largely from corn, grains, sugar and sucrose materials as well as other starch-rich crops. Precisely, in the United States of America, Brazil and China where over 75% of the total ethanol used globally are produced (IEA, 2016), production of ethanol is mainly from corn,

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sugarcane and grains. These materials are important food items in every home and also significant raw materials to major food and beverage companies. As such, continued production of fuel ethanol from the materials is unsustainable and detrimental to balance nutrition as well as the global food security program especially in Sub-Saharan Africa where there is malnutrition and about 72% of the population still live below 1 dollar per day (UNDP, 2015). To this effect, the drift to use non-food materials for biofuels production has to be reinvigorated and sustained in order to achieve a climate resilient biofuels program and food security simultaneously.

Lignocellulosic biomass(s) such as oil-palm residues and wastes from forest/ sawmill operations are part of an important cellulosic resource which is yet to be fully utilized in energy production. These are non-food materials (Sa'ñchez *et al.*, 2008) and in fact currently represent an issue for environmental concern due to uncontrolled dumping as a means of disposal (Abikoye *et al.*, 2014). This situation mostly leads to degradation of lands as well as contamination of surface and underground water. In addition, air pollution has also been an issue as a result of incomplete combustion in cases where burning remains the only means to get rid of the biomass. Whereas these materials are majorly made up of cellulose, hemicellulose, lignin and slight trace of extractives and other inorganic materials which could be processed to fermentable sugars for producing biofuels (Avci *et al.*, 2013; Saini *et al.*, 2014). Other lignocellulose biomass(s) which are also available in abundance include: crop residues, municipal solid wastes and large fraction of manures (Sa'ñchez *et al.*, 2008; Saini *et al.* 2014).

It is good to mention at this point that the possibility of converting lignocellulosic biomass to useful products through either chemical, biological or biochemical processes has long been established (Chesson *et al.*, 1988). According to Galbe *et al.*, (2002), Mustafa *et al.*, (2008), and Abikoye *et al.*, (2014), the major operations that suffice for modern conversion of lignocellulose biomass to ethanol and other value-added cellulosic products include: (1) pre-treatment of biomass and hydrolysis of cellulose and hemicellulose to mono-sugars (2) fermentation of the various sugar complexes to ethanol (4) capturing of lignin components and (4) purification/refining of the ethanol formed. While the hemicellulose fraction of the complex is a collection of linear and branched hetero-polymers of D-xylose, L-arabinose, D-galactose, D-glucose and D-mannose structure (figure 2) which are easier to breakdown or hydrolyse, cellulose is a complex linear and crystalline polymer of β -D-glucose unit (figure 1) which is difficult to break due to their crystalline structure (Chang *et al.*, 2000; Mosier *et al.* 2005). The lignin fractions on the other hand are entrenched within the complex as a three-dimensional polymer molecule that contains three different phenyl-propane precursor monomer units (figure 3) which are predominantly too tough for biodegradation and therefore remains the most recalcitrant among the various components of the biomass (Palonen, 2004).

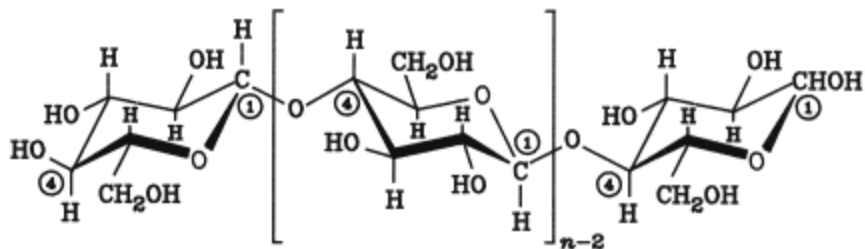


Figure 1: Structure of single cellulose molecule

Over the years, the techno-economic performance of ethanol production from lignocellulosic materials via these major processing routes have been put to tests. One area which is commonly examined due to its overall importance is how to improve the rate of biomass conversion and ethanol yield from the materials (Saini *et al.* 2014). In this regard, surface area, particle size and porosity of the biomass materials have been recognized to play key roles during hydrolysis. Hence, biomass pre-treatment (which is the unit operation that captures all these features) is often described as the most critical stage that determines the degree to which the biomass will be accessible to either chemical, biological or biochemical degradation (Piccolo *et al.*, 2009).

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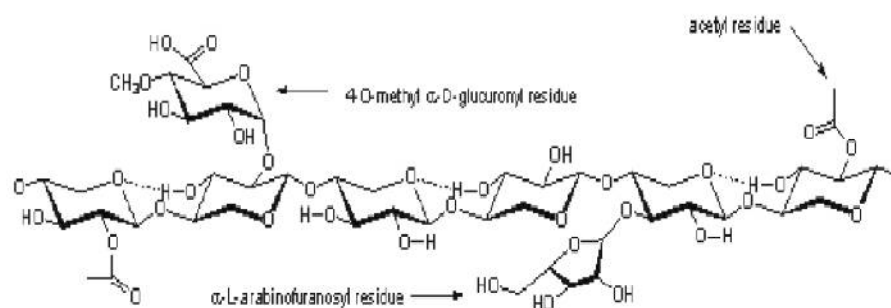


Figure 2: Representation and structure of the hemicellulose

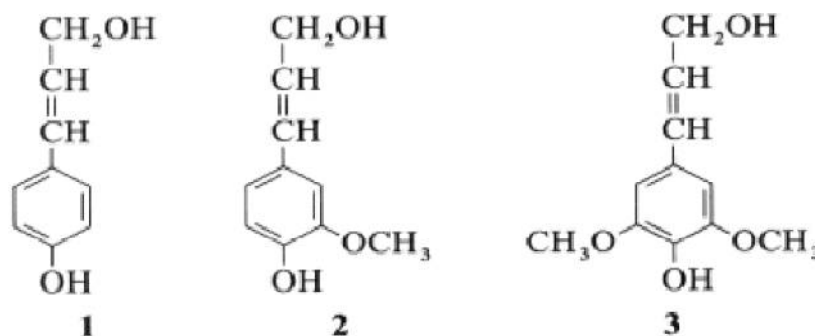


Figure 3: Schematic structure of P-coumaryl-, coniferyl- and sinapyl alcohol: dominant building blocks of the three-dimensional polymer lignin

Several biomass pre-treatment methods/technologies have been examined on different types of lignocellulose biomass (Tahezadeh *et al.*, 2008; Alvira *et al.*, 2010) with each showing varying results with respect to material source and process conditions (Geddes *et al.*, 2011). According to Devendra *et al.*, (2015), the observed variation obtained from different study results could be attributed to disparities in morphological structures and physico-chemical properties of the biomass(es). This implies that among the various pre-treatment considerations, none could be described as “the best or front-runner” since each of them has its unique benefits and limitations. However, despite the varied result and seemingly different level of performance, the main goal in every biomass pre-treatment operation is to decrystallize and depolymerize the cellulose and hemicellulose fractions of the biomass and to alter the lignin structure so as to ensure rapid biomass hydrolysis and improved product yield. This paper presents a review of some major pre-treatment methods used in the conversion of lignocellulose biomass to mono-sugars, ethanol and other biomaterials. The purpose of the review is to come up with an efficient bioprocess for converting a mix-feed of oil palm residues and sawmill wastes materials to bioethanol in a manner that is environmentally sustainable and cost effective and also limit the formation of inhibitors as by-product during hydrolysis.

II. BIOMASS PRE-TREATMENT METHODS

As mentioned in the previous section, pre-treatment has been identified as the crucial step in biomass processing. Consequently, it is also the most expensive stage in biofuels production (Mosier *et al.*, 2005; Carvalho *et al.*, 2008; Alvira *et al.* 2009). According to Tahezadeh *et al.* (2007), the general biomass handling techniques and preparation for

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hydrolysis and fermentation processes can be classified under physical, chemical and biological pre-treatments with respect to the mechanisms and different forces involved as well as the type of energy employed. Other methods that combine two or more of these pre-treatment techniques also exist and they have been classified following the same nomenclature in line with the number of techniques that are combined (McMillan, 1994; Hsu, 1996; Devendra et al., 2015). The major group for categorization are discussed in following sections.

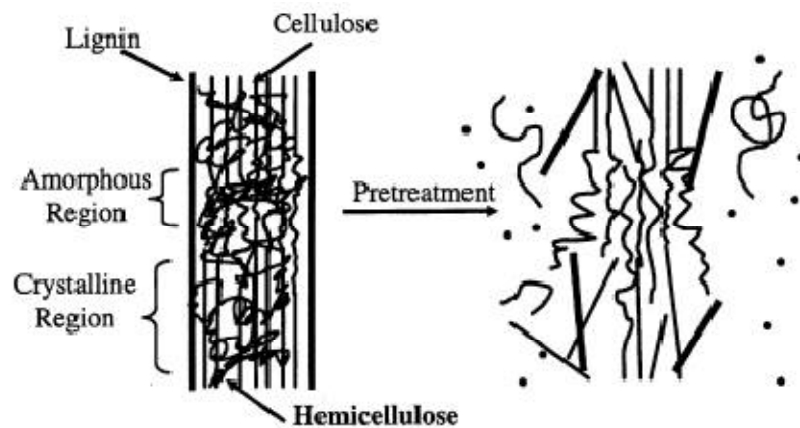


Figure 4: Schematic description of the effects of pre-treatment on lignocellulosic biomass (Adapted from Hsu et al., 1980)

Physical Pre-treatments

Physical pre-treatment method does not make use of chemicals, reagents or catalyst. There are many types of physical pre-treatment, however the major ones include mechanical comminution (milling, grinding and chipping), extrusion, high energy radiation, hot water pre-treatment and uncatalyzed steam explosion. Methods that are considered in this review are mechanical comminution, extrusion and steam explosion.

Mechanical Comminution

The process of mechanical comminution breaks down the biomass to smaller particle sizes through mechanical processes. This disrupts the crystalline structure of the cellulose and increases surface area of the biomass thereby decreasing the degree of polymerization within the structure, making the materials more accessible to hydrolysis enzymes and chemicals. There are various forms of mechanical comminution including chipping, pelleting, compression, grinding and milling. Milling could be by hammer milling, ball milling or vibrating rod milling while the operation could either be wet or dry depending on the nature of biomass, intended purpose of use and prevailing weather condition. Biomass pre-treatment involving some of these technologies have been reported in literature (Zhang et al., 2007; Yoshida et al., 2008), early researchers found that vibratory ball milling are more effective when compared with ordinary ball milling with regards to making biomass accessible for digestion (Millet et al., 1976; Ryu et al., 1983). Hsu, (1996) reported the successful use of compression method of milling in large scale/commercial production of bioethanol. However, it is essential to state that mechanical comminution does not isolate or remove lignin components (which mostly act as restriction to chemical and enzyme actions during) from the biomass. Hence, it is always recommended to use the method in combination with other types of pre-treatment strategies so as to achieve efficient pre-treatment process.

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Extrusion

The process of extrusion has to do with the treatment of biomass materials at a temperature of 300°C and above followed by mixing and shearing of the heated fractions. This results in both physical and chemical restructuring of the cellulose and other part of the complexes (Zheng *et al.* 2014). According to a study conducted to monitor the influence of high shear bioreactor parameters on the release of carbohydrate from different biomasses, Karunanithy *et al.*, (2008) observed that for every extrusion studied, screw speed and barrel temperature are the major factors that determine the efficiency of the process. This is because they are responsible for disruption of the biomass structure leading to fibrillation, defibrillation and fibre shortening increases the exposure of the materials to enzymes attack.

Steam explosion (uncatalyzed steam explosion) or autohydrolysis

This is a method of biomass pre-treatment in which only steam water is used. The method is characterized by rapid heating of the biomass by high-pressure steam over a period of time to enhance the hydrolysis of hemicellulose and subsequent termination of the process through swift (rapid) release of the pressure. This makes the biomass to undergo rapid compression and explosive decomposition. According to Avellar *et al.*, (1998) and Devendra *et al.*, (2015), steam explosion pre-treatment is more attractive than other methods of biomass pre-treatment because it is cost effective, possesses more potential for energy efficiency, less hazardous and with little environmental footprint. Many school of thoughts have classified this method as a physico-chemical process because of the formation/release of acetic acids as well as other acids from acetyl functional groups which are often released by the biomass thereby initiating autohydrolysis of the hemicellulose at high temperature. In addition to that, it has also been reported that at a very high temperature, water possesses some acidic properties which further catalyse the hemicellulose hydrolysis (Pan *et al.*, 2005). Hence, steam explosion pre-treatment is essentially a combination a mechanical forces and chemical effects. Other pre-treatment methods that have been verified under this classification include liquid hot water pre-treatment (Brandon *et al.*, 2008; Rogalinski *et al.*, 2008) and High energy radiation (Imai *et al.*, 2004; Yang *et al.*, 2008).

Chemical Pre-treatments

Chemical pre-treatment methods are those biomass conditioning processes that utilize chemicals and reagents in their operation. In this method, the biomass is crushed to smaller piece and then submerged in the dissolving solution at specific temperatures over a period of time. Most chemical pre-treatments processes that have been considered in ethanol production using agricultural biomass as feedstock were formulated to enhance cellulose biodegradability through the removal of the lignin fractions and also to reduce the degree of polymerization of cellulose fractions contained within the biomass(s). Notable chemical pre-treatment techniques include: Acid, Alkaline, Ammonia, ionic liquids, oxidative, ozonolysis, CO₂ explosion, organosolv and catalyzed steam explosion pre-treatment methods. However, this study mainly examines few of these techniques that are commonly been used for forest and agricultural residue pre-treatments.

Acid Pre-treatment

In this method, the dissolving agent is an acid. Here the milled biomass is either initially soaked in water before acid hydrolysis or directly submerged in the acid solution through a desired period. This process is generation followed by separation through filtration to remove the unhydrolysed solid substrate. Generally, the more negative an acid pKa value is determines how effective the acid hydrolysis process will be because the concentration of the hydrogen ion is directly linked to the hydrolysis reaction constant (Bobleter, (1994); Bensah *et al.*, 2013). During acidic pre-treatment process, amorphous hemicelluloses fractions contained in the lignocellulose biomass tend to hydrolyse to soluble sugars faster than the cellulose counterpart especially in mild conditions. This according to Chen *et al.*, (2012), via the disruption of xylosidic bonds and cleavage of acetyl ester groups while the enclosure of lignin bonding with the complexes is dislodged and degraded through substitution reactions breaking the links associated by condensation reactions that prevent dissolution (Pingali *et al.*, 2010; Candido *et al.*, 2012). Cellulose on the other hand are dissolved through the preferential degradation of amorphous sections which lead to the enlargement of cellulose fibrils that increases the crystallinity index of pre-treated biomass.

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The rate of acid hydrolysis process is usually affected by the concentration of the acid, liquid to solid ratio, temperature of the medium, particle size and resident time. However, according to *Chum et al., (1990)*, the unified factor (combined severity factor, R_0^i) is normally been used to assess the effect of temperature, pH and time on efficiency of the acid pre-treatment process.

$$\text{Log } R_0^i = \log (t \cdot e^{(T-100)/14.75}) - \text{pH}$$

Where T is the hydrolysis temperature in °C and t is the reaction time in minutes (*Chum et al., 1990*).

It is worth mentioning that acid hydrolysis can be further classified as dilute and concentrated acid hydrolysis depending on the concentration and type of acid used. A comprehensive review on this distinction has been presented in literature, readers are referred to by *Bensah et al., (2013)* for more details on this categorization.

Alkali pre-treatments

The major importance of Alkali pre-treatment is the removal of lignin from the biomass complexes which leads to improvement in the reactivity of polysaccharides that remain. During this process, biomass is usually treated with major alkali such as calcium potassium sodium and ammonium at room temperature and normal pressure. Uronic acid and other acetyl groups available within the hemicellulose fraction are removed during this process thereby enhancing their accessibility to enzymes during hemicellulose degradation. According to (*Sun et al., 2002*) and (*Chang et al., 2000*), the Ester connections between xylan and hemicelluloses are also hydrolysed during this process. Summarily, the general mechanism in alkaline pre-treatment involves the mixture of lignocellulose materials with bases (i.e. as aforementioned) at normal or specified temperatures and pressures so as to degrade the glycosidic and ester side chains within the materials. This results in disruption of the lignin structure as well as cellulose decrystallization producing two major components of wet solid cellulose and the liquid fraction which is made up of dissolved hemicelluloses, lignin, and unreacted inorganic chemicals (*Conde-Mejía et al., 2012; Yoo et al., 2012*).

Ammonia Pre-treatment

The techniques of ammonia pre-treatment encompass the ammonia fibre explosion-method commonly referred to as (AFEX), soaking and submerging in aqueous ammonia and ammonia recycle percolation (ARP). In this type of pre-treatment, biomass is treated with aqueous ammonia at elevated temperatures. While cellulose decrystallization occur through the process, the elevated temperatures reduce the lignin content and also removes some hemicellulose fraction during the process. The general ammonia pre-treatment is in the real sense an alkaline treatment but due to the effectiveness of the method especially in the treatment of herbaceous materials and agricultural wastes, it is widely recognized as a distinct process and as such treated as a separate method. Whereas submerging the biomass materials in aqueous ammonia (i.e. SAA) removes lignin efficiently at a very low temperature, the ARP requires liquid flow through a column reactor at higher temperature. A detail overview of all ammonia pre-treatment techniques has been presented by *Harmsen et al., (2010)* and readers are referred to the paper for details about this review.

Biological Pre-treatment

In biological pre-treatment process, the biomass residues are degraded by microorganisms like white-, brown-, soft rot fungi and some bacterial in order to restructure the chemical composition of the biomass so as to make them more exposed to enzymatic digestion. The rate of degradation during biological pre-treatment is usually slow and occurring over a long residence time. However, the consolation to this drawback is the that biological pre-treatment requires a very low energy input as well as mild operating conditions (*Sun et al., 2002*). According to *Ander et al., (1978)*, *Lee et al., (2007)* and *Boonsawang et al., (2012)*, the effects of brown and soft rots fungi on lignin is not pronounced but their major attack is on the cellulose complexes while the action of the white-rot fungi are mainly to on lignin degradation. Conventionally, many of these pre-treatment methods do not occur in isolation. More often than none, they go 'Pari Passu' with each other and are therefore classified following the order of their combination i.e. Biochemical for

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biological and chemical pre-treatments, Physicochemical for physical and chemical pre-treatments and several other classifications ().

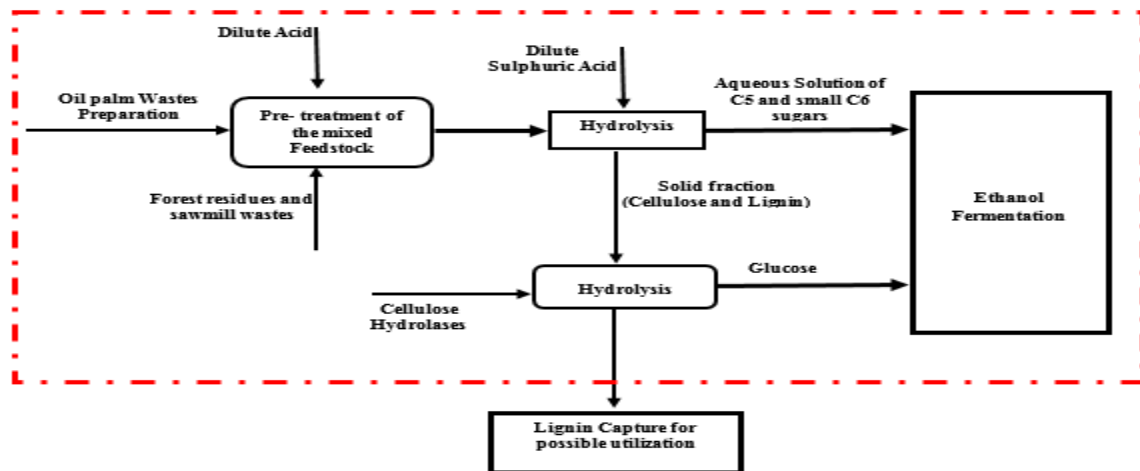


Figure 5: process flow and experiment procedure for converting oil palm and wood wastes to Bioethanol

III. CONCLUSIONS AND FUTURE RESEARCH OUTLOOK

Extensive research works have been carried out to improve process(s) involved in the production of liquid fuels from lignocellulosic biomass. These methods have been applied to the hydrolysis of feedstock obtained from a single crop (either homogenised from the residues of a particular crop or waste materials of different crops which are processed separately). The limitation to these applications lies in the fact that the unfolding challenges of global climate change, environmental concerns and complex water-food-energy nexus, requires increased production of alternative liquid transportation fuel to substitute the carbon-intensive petroleum products and other fossil fuels which is constrained by the seasonal variability of different lignocellulosic biomass base-crops across the year. Hence, there is need to pursue a bioprocess conversion pathway that can handle the hydrolysis and subsequent fermentation of mix-feed of biomass residues. This will ensure multi-period sustainability of the biofuel processing plants all-year round with respect to feedstock availability. Furthermore, it is the author's opinion that such an ideal procedure might require the combination more than one biomass pre-treatment techniques which must be fitted to a single process loop in order to minimize total cost and environmental impact. More so, this method should also factor-in an approach to find the trade-off among these aforementioned objectives with water/chemical utilization and recovery in a systematic manner. Hence there is need to develop an optimal and effective bioprocessing method that takes into account all the attributes highlighted above in the production of cellulosic ethanol from a mix-feed of oil palm residues and forest/sawmill wastes. It is envisaged that the method will lead to increased product yield and promote economic attractiveness of the biofuels industry through cost minimization and improved material recovery.

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