

Oil Palm Biomass Pretreatment and Hydrolysis: A Recent Biotechnological Venture Towards Bio-Based Lactic Acid Production

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ABSTRACT

The effective utilisation of lignocellulosic biomass as fossil-based counterparts in the development of bio-based chemicals manufacturing is progressively relevant. Hence, many works are underway to shift from petrochemical industries to a sustainable lignocellulosic biomass biorefinery in lactic acid production. Malaysia is the leading country as a palm oil producer, with an enormous supply of inexpensive, renewable and non-food, yet untapped oil palm biomass resources. In this regard, oil palm fronds (OPF) rich in glucan content account for 60% of total agricultural biomass in Malaysia, which can accommodate 2 million metric tons per annum of fermentable sugar. The richness of carbohydrates in OPF serves as the key to unlocking bio-based lactic acid commercialization for future sustainable breakthroughs. This paper aims to provide insights into the exploitation of OPF as the novel feedstocks in bio-refinery processes. Special emphasis in this review is put on the technology, global demand, commercial status and future prospects of the production of second-generation lactic acid, as this process has received most research and development efforts so far. It reviews the current research attributed to the compositional analysis of OPF by primarily focusing on the National Renewable Energy Laboratories (NREL) protocol. It then focuses on the recent technological advancements of different pretreatment methods and hydrolysis for carbohydrate recovery in lactic acid production. Given with the tremendous potential, OPF can be exploited as an excellent sugar platform for the production of higher value products such as advanced biofuels, fine-platform chemicals and bioenergy.

Keywords: Oil palm frond; lactic acid; pretreatment; enzymatic hydrolysis

INTRODUCTION

Nature supplies an abundance of biomass resources that could serve as potential feedstock in the bioconversion processes. Biomass conversion technologies are gaining a considerable momentum since it is a clean, sustainable, and renewable energy source for the production of diversified bio-based fine chemicals (Dessie et al. 2018).

Lactic acid is a vital naturally occurring hydrocarboxylic acid metabolite in various organisms, from anaerobe microorganisms, plants, animals to humans (Yang et al. 2020). Given its usefulness in synthesising different essential industrial products such as a flavour enhancer acidifier, emulsifier, and preservative in food manufacturing and as an emulsifying and moisturising agent in cosmetics, as an intermediate in pharmaceuticals, and as production of solvents in the chemical industry (Mazzoli 2020). PURAC® is the world's largest lactic acid producer, accounting for approximately 45% of lactic acid production, with such

an installed capacity of roughly 350,000 tons per year (Hörhammer et al. 2014). By 2028, the global lactic acid market is expected to be worth USD 5.02 billion with an anticipated Compound Annual Growth Rate (CAGR) of 12.8% from 2021 to 2025, where it has been widely applied in various industries such as the manufacturing of food and beverages and pharmaceuticals, particularly in developing economies in India, China, and Indonesia. Furthermore, the market growth is due to the demand for the feedstock in polylactic acid (PLA) production (Din et al. 2021).

Bio-based lactic acid production by capnophilic bacteria is considered the best alternative to the petrochemical route (Q. Li et al. 2010) up to the final titers of 135.6 ± 0.14 gL⁻¹ with an overall yield of 0.96 ± 0.09 gg⁻¹ glucose and 2.94 ± 0.03 g L⁻¹ h⁻¹ productivity. The metabolites at the end of dual-phase fermentation by 130ZT were (in parentheses: the mol end product formed/100 mol glucose. It is in line with the mission of the United Nations Framework Convention on Climate Change to reduce carbon footprint using green

technology in producing green chemicals (Tan et al. 2017). A life cycle analysis done by The Ohio State University shows a 50% reduction in greenhouse gas (GHG) emissions and over 50% reduction in fossil fuel consumption for bio-based chemical compared to fossil-based chemical. According to Lactic Acid Market report, bio-based lactic acid consumption offers 75% carbon footprint reduction reflecting its ability to overcome sustainability and environmental problems (Lactic Acid Market 2020).

HISTORICAL PERSPECTIVES OF LACTIC ACID PRODUCTION

Lactic acid (2-hydroxy-propanoic acid) is a chiral carboxylic acid and a key metabolic intermediary in many species, from anaerobic bacteria to humans (De Oliveira et al. 2020). It is one of the critical building-block chemicals with much reactivity due to an asymmetric carbon atom with two functional groups (-COOH) and has a chemical formula of $C_3H_6O_3$ (Chin et al. 2016). In 1780, lactic acid was identified in sour milk for the first time by Swedish chemist Scheele. Since then, Fremy experimented with lactic acid fermentation with various carbohydrates, including sugar, milk, starch, and dextrin. Pasteur recognised in 1857 that lactic acid was a metabolite released by particular microbes during fermentation, not a component of milk (Komesu et al. 2017). It has been long historically applied in the food and non-food industries, including the cosmetic and pharmaceutical industries, and synthesises oxygenated chemicals, plant growth regulators, and special chemical intermediates (Abdel-Rahman et al. 2011).

Traditional lactic acid is petrochemically produced from the hydrolysis of lactonitrile, base-catalysed degradation of sugars, and propylene glycol oxidation (Djukić-Vuković et al. 2019). However, the petrochemical approach is not favoured since it results in a racemic mixture of lactic acid and requires petrochemical resources (Abdel-Rahman et al. 2011). Therefore, the biochemical method is more favourable as high optical purity enantiomers of lactic acid can be obtained from fermentation, and the use of inexpensive renewable lignocellulosic biomass as feedstock increases environmental sustainability (Abdel-Rahman et al. 2021). Meanwhile, biochemical pathways approaching the maximum theoretical carbon yield became the main driver in replacing the petrochemical route. The method of fermentation to produce lactic acid from renewable sources can be a more efficient alternative in terms of greenhouse gas savings and optimum energy consumption while reducing dependence on limited mineral resources (Tan et al. 2018).

THEORY AND SIGNIFICANCE OF BIO-LACTIC ACID TECHNOLOGY

In the 1930s, bulk products such as fuels, organic acids and other essential chemicals were derived from biological sources (Ribeiro et al. 2018). The practice then goes hand in hand with developing various products from petrochemical industries that have dominated the world market, resulting in many biotechnology processes being replaced by chemical synthesis (Kilian 2016). Energy usage and other environmental aspects were not a critical issue at the time. However, by the 1970s, the first oil crisis has led to the process revisiting once again. The scenario is a complete indication that fossil resources are limited and not a perfect source to fuel combustion engines and power plants (Hosseini et al. 2017). Moreover, the market demand for durable and high-quality consumer goods is forecasted to increase by more than double in the near future (Benavides et al. 2020). Following this scenario, the chemical industry is now actively exploring alternative pathways of white biotechnology by exploiting renewable resources in producing platform chemicals (Chandel et al. 2020). These factors have also contributed to the use of microorganisms as biocatalyst of choice in producing 90% of the lactic acid market, such as Lactic acid-producing bacteria species including *Lactobacillus*, *Lactococcus*, *Streptococcus*, *Leuconostoc*, *Pediococcus*, *Carnobacterium*, *Aerococcus*, *Oenococcus*, *Tetragenococcus*, *Vagococcus*, *Weisella* and *Enterococcus* (Hatti-Kaul et al. 2018). However, rumen-type bacteria such as *Actinobacillus succinogenes* has been identified as one of the high titer lactic acid-producing strain via dual-phase fermentation by shifting the carbon flux pathway to lactate production (Q. Li et al. 2010) up to the final titers of 135.6 ± 0.14 g L⁻¹ with an overall yield of 0.96 ± 0.09 gg⁻¹ glucose and 2.94 ± 0.03 g L⁻¹ h⁻¹ productivity. The metabolites at the end of dual-phase fermentation by 130ZT were (in parentheses: the mol end product formed/100 mol glucose. *Actinobacillus succinogenes* (*A. succinogenes*) is a gram negative, pleomorphic and capnophilic bacterium, which requires excessive carbon dioxide for healthy cell growth (Luthfi et al. 2020). It also can use various types of carbon sources (Chiang et al. 2018). This phenomenon can indirectly create a sustainable biochemical process to help reduce GHG emissions (Luthfi et al. 2017). Based on a life cycle analysis, bio-lactic acid production recorded a net-zero carbon footprint and reduced 92% of total fossil resource-scarcity impacts compared to the petrochemical process (Ögmundarson et al. 2020). Lactic acid is a significant molecule can be formed in the metabolic pathway

of facultative anaerobic microorganisms (Wang et al. 2014). As shown in Figure 1, phosphoenolpyruvate (PEP) is produced by glycolysis of sugar and converted into pyruvate with lactic acid, acetic acid, formic acid and ethanol as the

final product in the C3 pathway or oxaloacetate, followed by the formation of succinic acid in the C4 pathway (McKinlay et al. 2008).

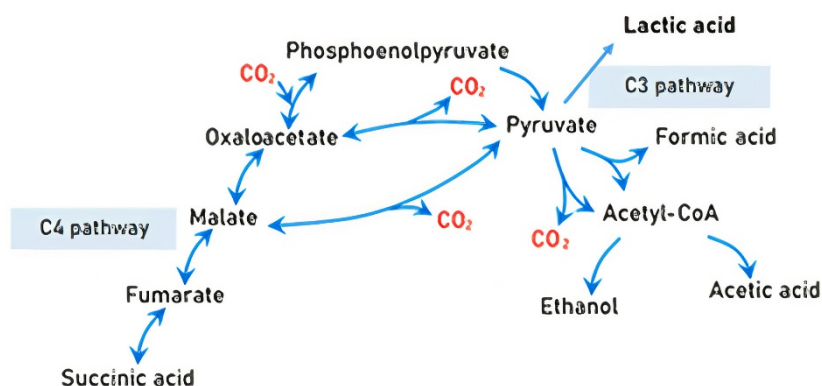


FIGURE 1. Metabolic pathway in the production of lactic acid

It is demonstrated that a lactate-forming C3 pathway is controlled by Pyruvate formate lyase 1-activating protein (pflA) and 6-lactate dehydrogenase (encoded LDH) to produce lactic acid (Zhang et al. 2019). LDH is the NADH-dependent catabolic enzyme that serves to reduce the pyruvate in order to produce lactic acid (Chroumpi et al. 2020; Novy et al. 2018). Accordingly, the addition of carbon dioxide leads to increased cell activity, yield and a final concentration of lactic acid (Wang et al. 2014).

Prospects of bio-lactic acid as platform chemicals are likely to generate lucrative income in addition to growing forecasted global market (Chandel et al. 2020). Lactic acid is identified by U.S. Department of Energy's National Laboratories as an excellent chemical platform for other fine-chemicals conversion including acrylic acid, propylene glycol, acetaldehyde, and 2,3-pentanedione and polymers such as poly-lactic acid (PLA) (Utilizing et al. 2020). The application of bio-lactic acid as precursor in the various sectors such as safe food supply, environment, industrial, recreation, housing, transportation, textiles, health and hygiene (Werpy et al. 2004). Polylactic Acid (PLA) is biodegradable bio-based plastic polymers synthesized from lactic acid (Grasa et al. 2021). Due to its high durability, renewability, compatibility, biodegradability and promising transparency, the use of PLA has received a great interest and stood up as the prominent ideal bio-based chemicals replacing the conventional fossil-based products (Abdel-Rahman et al. 2021; Puiggali et al. 2017).

CURRENT MARKETABLE PRODUCT BASED ON BIO-LACTIC ACID

The bio-lactic acid production now can accommodate large quantities about 350,000 tons per annum, with lower current market prices between USD \$1.7 and 2.1 kg⁻¹ which is adequate to substitute 30% of U.S petroleum consumption (Y. Li et al. 2021). Research towards optimizing biochemical processes is still underway for more economical lactic acid production. In recent years, several major companies from different countries such as NatureWorks LLC (United States), Archer Daniels Midland Company (United States), Purac (The Netherlands) and Galactic S.A. (Belgium) are emerging and actively engaged in commercializing bio-lactic acid based products as new commodities (Cubas-Cano et al. 2018). The market of Corbion-Purac are comprised of 74.2% net sales of bakery products, 23.4% of biochemical supplies and 2.4% others across all of its production plants in the USA, The Netherlands, Spain, Brazil, and Thailand (Hörhammer et al. 2014). NatureWorks LLC is one of the leading company in lactic acid production with the brand Ingeo™. It can accommodate 140,000 metric tons of Ingeo™ biopolymer for various applications such as safe food packaging, health and personal care, home appliances and 3D printing filament (Alves de Oliveira et al. 2018). To date, majority of the companies utilise crop sugars such as sugarcane, yeast extract, cassava, sweet sorghum, potato, wheat, rye-barley, rice, xylan, and galactan as lactic acid feedstock. Food security issue may arise in order to meet the

global growing demand of lactic acid production. Hence, lignocellulosic material from biomass is foreseen as an ideal feedstock alternative for the lactic acid production due to its low price, sustainable, and high in sugar content yet non-food abundance, hence securing global food availability.

OIL PALM BIOMASS POTENTIAL

Malaysia is a tropical country where the palm oil industry is among the fastest-growing vegetable oil sector and has positively impacted socioeconomic development in the Southeast Asian region (Ata et al. 2015; Sumathi et al. 2008). It happens due to the factor of biofuels development in the European Union (EU) and a striking demand from Indonesia, India and China (Sumathi et al. 2008).

Oil palm trees (*Elaeis guineensis*) generally bear fruit within 2.5 years after they are grown and their economic life span is approximately 25-30 years before replanting (Luskin & Potts, 2011; Sumathi et al. 2008). On average, a palm tree with a maximum height of up to 20 m has about 40 palm fronds. The leaf is shaped like a comb, while the stalk can reach up to 7 m long (Dewi et al. 2018). In Malaysia, palm trees are planted with a total area of more than 4.6 million hectares (Ng et al. 2012). Extracted oils are used for food and related industries or as raw materials for producing detergents and cosmetics (Yamada et al. 2010). Moreover, about 90 million tonnes of solid biomass from the palm industry are produced annually, including palm shells, mesocarp fibres, empty fruit bunches, palm kernels, fronds, and trunks (Loh, 2017; Saba et al. 2015).

Previous researches reported that average carbohydrates in solid oil palm biomass contain about 58-66% of the total initial dry weight (Jung et al. 2012; Tan et al. 2016), where it comprises repeating units of glucose, mannose, xylose and arabinose (Goh et al. 2010). Carbohydrate molecules found in plant cell walls are shielded by lignin through covalent bonds, thus reducing cellulose or hemicellulose accessible surface area for enzymatic attacks (Zhang et al. 2015).

The residual agro-industrial waste can be converted into carbon sources for the production of lactic acid. According to Tan et al. (2016), OPF comprises 75% solid fraction, while another 25% is its juice. Cellulose and hemicellulose content in OPF is 41.7% and 16.4%, respectively, based on dry biomass weight (Zahari et al. 2012). The conversion of OPF into value-added product lactic acid will be a strategic step for the palm oil industry to champion zero-waste technology through effective cellulose and hemicellulosic waste management system. Moreover, the high content of carbohydrates in OPF has been shown to potentially be converted to bioethanol (Goh et al. 2010; Hong et al. 2012), biohydrogen (Yasin et al. 2013), bio-butanol (Loyarkat et al. 2015), polyhydroxybutyrate (Zahari et al. 2012), and xylitol (Manaf et al. 2018). However, the use of OPF as a sustainable raw material in biochemical production is still in its early stages and requires further development.

Monomeric sugars such as glucose and xylose are obtained from biomass through two bioprocessing steps, namely pretreatment (or pre-hydrolysis) and enzymatic hydrolysis (Alvira et al. 2010; Talebnia et al. 2010). Pretreatment removes lignin and silica and treat the cellulose-hemicellulose matrices' whole structure to facilitate the enzyme accessibility to the targeted substrate (Zakaria et al. 2015). Accordingly, Novozymes, with the National Renewable Energy Laboratory (NREL), has combined effort to develop recyclable enzymes with high activity and protein concentration to promote the use of environmentally friendly solvents (Aden & Foust, 2009; Himmel et al. 2007; Rodrigues et al. 2015). A high concentration of hydrolysed sugar can then be used as feedstock in the sustainable production of lactic acid (Luthfi et al. 2016).

LIGNOCELLULOSIC MATERIALS AS SUSTAINABLE FEEDSTOCK

Lignocellulosic biomass is a renewable source of raw material, where it comprises cellulose, hemicellulose, and lignin as major components. The potential of these biopolymers as sustainable raw materials has not been fully realized due to historical shifting from biomass to the exploitation of crude petroleum since the 1940s (Halvorson, 2011). Another factor is the complex structure of lignocellulose with limited solvent availability (Sun et al. 2011). When the carbohydrates contained in biomass can be dissolved efficiently, they can potentially be converted into chemicals and fuels through catalytic, fermentation or other pathways (Jung et al. 2012; Wang et al. 2014).

Lignocellulosic materials contain up to 70% of the total structural carbohydrates comprising cellulose and hemicellulose (Brandt et al. 2013). In cellulose, linear chains of glucose molecules are bound together through $\beta(1 \rightarrow 4)$ glycosidic bonds (Li et al. 2020). Cellulose is a very stable carbohydrate consisting of 2,000 to 12,000 glucose units (Hidayat, 2018). This polysaccharide has a chemical formula $(C_6H_{10}O_5)_n$ and is primarily composed of (1,4)-D-glucopyranose units that form $\beta(1 \rightarrow 4)$ networks. Raw lignocellulosic materials typically contain about 40-50% cellulose bound with hydrogen bonds (Anwar et al. 2014). However, it tends to form hydrogen bonds between molecules that maintain the integrity of the material structure. It makes this polymer hydrophobic or organic solvent resistant. Cellulose molecules are present in most forms of macromolecular conformation that can generally be classified as crystalline or amorphous forms. Cellulose crystals require more energy to be hydrolyzed than amorphous cellulose (Anwar et al. 2014; Krasznai et al. 2018; Taherzadeh & Karimi 2008).

Hemicellulose is a heterogeneous biopolymer consisting of glucuronoxylan, glucomannan and some other polysaccharides. Hardwood or herbal plants usually contain glucuronoxylan, while glucomannan is more common in softwood (Girio et al. 2012). Galactan, arabinan and arabinogalactan are also included in the hemicellulose

group; however, they do not share the spine structure bound by $\beta(1 \rightarrow 4)$ bonds. Glucuronoxylan (O-acetyl-4-O-methyl-glucurono- β -D-xylan) contains xilopyranose as the hemicellulose spine and bonded through the $\beta(1 \rightarrow 4)$ tissue (Girio et al. 2012). Most agricultural wastes contain about 25-35% hemicellulose (Anwar et al. 2014).

Lignin also consists of aryl ether (α -O-4 'and β -O-4'), phenylcoumaran (β -5'), biphenyl (5-5'), resinol (β - β ') or diaryl propane (β -1') which binds three monolignol components, i.e. p-coumaril alcohol, coniferous alcohol and synapyl alcohol (Anwar et al. 2014). It has long-chain linkage and is a heterogeneous polymer which is a significant support structure in tissue vascular plants and some species of algae. Lignin is particularly important in forming cell walls, especially in plant and skin wood, as it provides the rigidity and resilience of the plant's internal biomass structure (Sun 2010). Lignin is a phenolic polymer that fills the cell wall space between cellulose, hemicellulose and pectin components. It is covalently bound with hemicellulose, thus providing mechanical strength to the plant cell wall (Anwar et al. 2014). Due to the branched and irregular structure formed by the random radicalization of phenol oxidative, the lignin layer surrounding the plant fibres is seen as an inhibitor of structural carbohydrates in biomass (Chou, 2016). In Malaysia, lignocellulose biomass from the oil palm source can be considered as a sustainable raw material for the conversion of value-added bioproducts such as methane, bio-plastic, sugar, organic acids, fertilizers, boards, activated carbon and livestock feed (Fatin et al. 2017; Hong et al. 2012; Tan et al. 2017; Zakaria et al. 2015). Even palm oil mill effluents can be converted to produce energy for electricity generation (Maaroff et al. 2018). Lignocellulose biomass such as OPF was collected during palm trees' replanting process in the old estate (Yamada et al. 2010). OPF are available daily throughout the year when trees are trimmed during the harvesting of fresh fruit bunches to extract oil (Loh, 2017). Empty fruit bunches fibres, mesocarp fibres and palm shells are collected during extraction of oil from sterilized fruits. Among these oil palm biomass, OPF are the most abundant biomass with annual availability of almost 60% out of 90 million tonnes of industrial palm waste (Lim, 2010; Puspasari et al. 2018).

Initial characterization techniques such as dietary fibre estimate the plant's relative digestibility and different substances after its intake by ruminants or humans (Prosky et al. 1988). It involves an enzyme-gravimetric method that can hydrolyze food samples with digestive enzymes after removing the fat content. After that, hydrolyzed carbohydrates are separated by precipitation and filtration, while proteins and inorganic substances are determined gravimetrically (McCleary et al. 2010). In 1999, acetyl bromide was developed for the analysis of lignocellulose material. In this method, lignin was dissolved and reacted with bromine, followed by the reductive and acetylated division (Krasznai et al. 2018). The resulting generic product is determined using spectrometry (Moreira-Vilar et al. 2014).

Over the years, several empirical techniques have continued to evolve toward a holistic approach in determining the chemical composition of lignocellulose materials such as oil palm biomass. The use of modern spectrometer techniques and modern chemometric techniques is a faster, safer and economical alternative tool (Krasznai et al. 2018). The combined process of gravimetric and instrumental methods in biomass composition analysis is required to account for extractives, structural carbohydrates, lignins, proteins, and ash in palm oil (Sluiter et al. 2010). However, the characterization method requires skill in calculating each component separately without repeating calculations (Krasznai et al. 2018). Figure 2 outlines the methods/protocols established for biomass characterization in different years.

BIOMASS COMPOSITIONAL ANALYSIS

The biomass compositional analysis is critical to study the effects of pretreatment and changes in lignocellulose material caused by various factors. In addition, it is necessary to analyze the component balance around the operating unit, the determination of the process yield and assessing the economic feasibility of bioconversion (Templeton et al. 2016). Some characterization protocols have been developed over the past ten centuries to characterize the structure and pattern of composition affecting the processing of lignocellulose materials. These methods depend on the goals and types of biomass used (Krasznai et al. 2018).

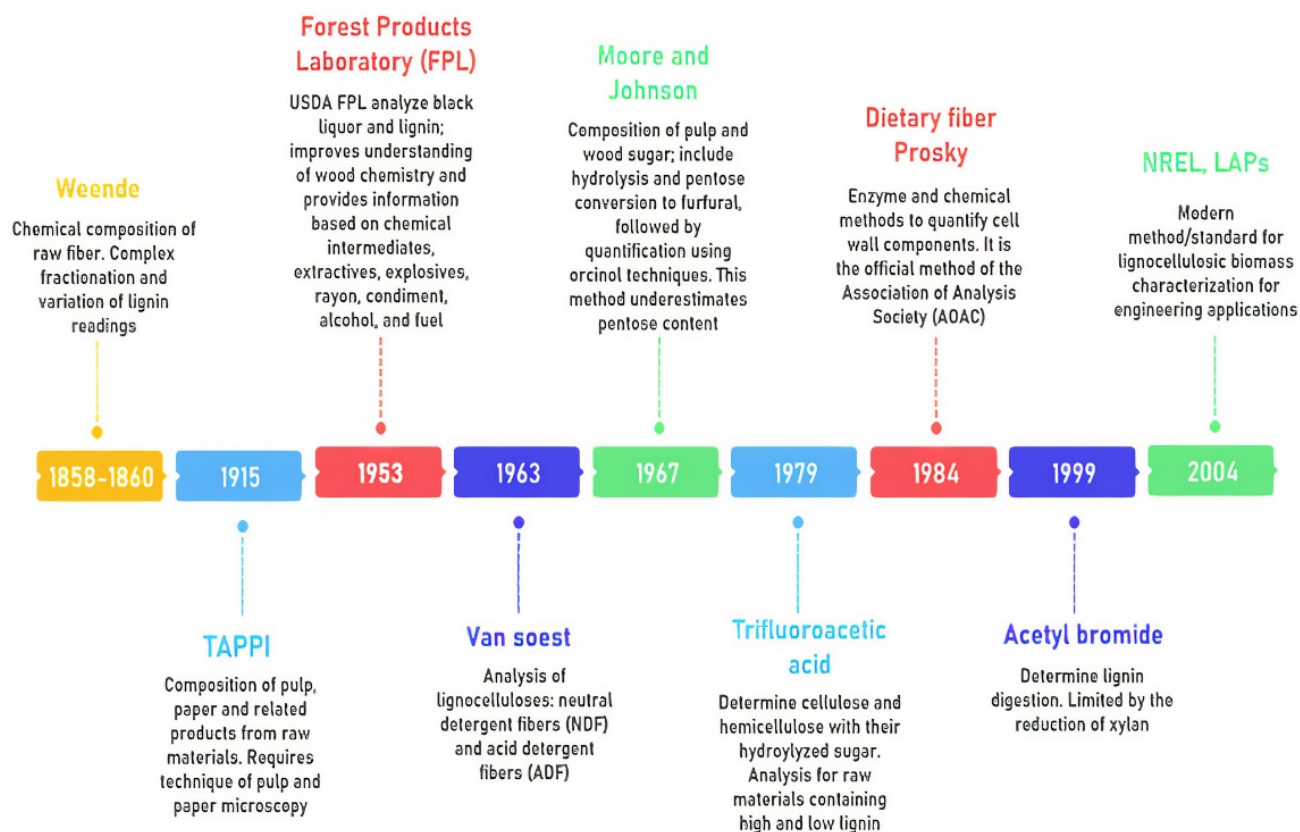


FIGURE 2. Methods for biomass characterization in different years

There are several methods of biomass analysis that are still used in different ways and objectives. However, all of these methods result from improvements from previous methods, as shown in Figure 2 (Krasznai et al. 2018). Among them are neutral detergent fibres (NDF) or acid detergent fibres (ADF) for the determination of lignocellulosic biomass composition (Zahari et al. 2012), hydrolysis techniques with trifluoroacetic acid or hydrochloric acid to identify carbohydrate networks (Foyle et al. 2007) and the technique of acetyl bromide or thioglycolate (Moreira-Vilar et al. 2014). These techniques are closely related to the Technical Association of the Pulp and Paper Industry (TAPPI) to determine lignin and holocellulose in the process of pulp and paper making (Krasznai et al. 2018). Each technique developed is relevant to the needs of each industry. Meanwhile, the Weende method is still used routinely in the agricultural sector (Krasznai et al. 2018). By far, the National Renewable Energy Laboratory (NREL) and TAPPI methods are the most well-known method of producing accurate and reliable results for biomass compositional analysis (Cuaya et al. 2014).

The method of analysis involving sulfuric acid has interrelated and empirical steps because a slight modification of the calculation technique or the adjustment of the component values may affect the final result (Foyle et al. 2007). This method, however, produces variable results due to differences in analyzer, laboratory and incorporated technique (Cuaya et al. 2014). Several laboratory analytical procedures (LAPs) developed in NREL are based on lignin isolation using sulfuric acid to determine the complete composition of lignocellulosic biomass (Tan et al. 2016). This method is carried out in stages. It involves the extraction of fibres using accelerated solvent extractor (ASE) and hydrolysis of two-stage sulfuric acid, followed by vacuum filtration to determine the content of lignin and phenolic compounds (Hames 2009; Sluiter et al. 2010). Figure 3 shows a flowchart summary of LAPs techniques developed in NREL to analyze the lignocellulose biomass composition.

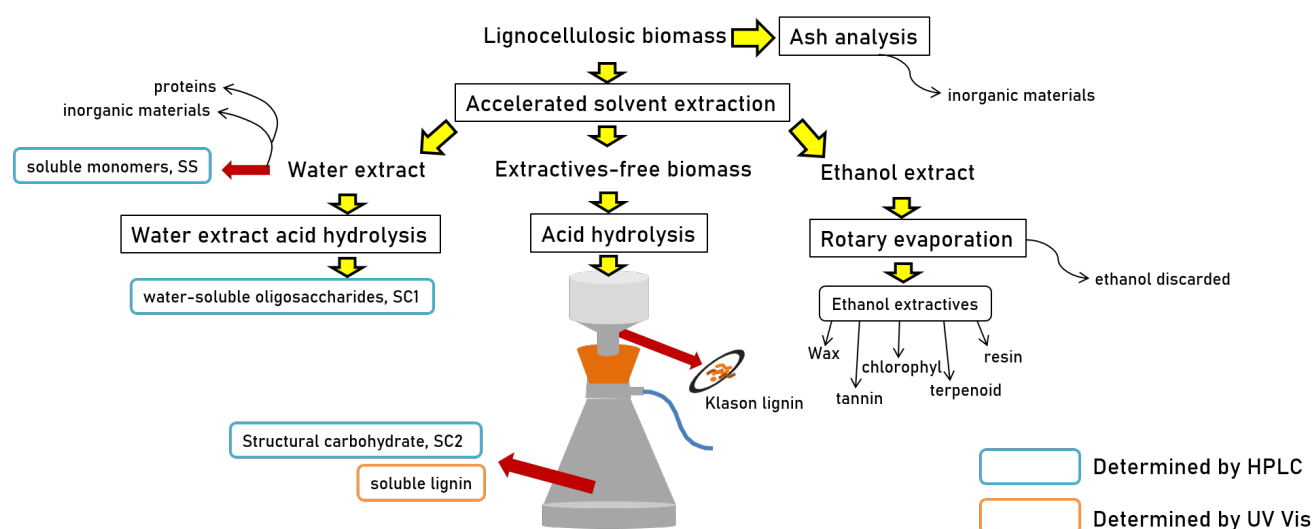


FIGURE 3. Flowchart summary of LAPs techniques developed in NREL

NREL's methods can be considered reliable guidelines for most types of biomass, especially woody materials and some herbaceous plants (Templeton et al. 2016). This standard analysis method helps determine the chemical composition of raw or treated oil palm biomass for conversion to bioproducts. It can also be used to assess the economic potential and its impact on the environment (Sluiter et al. 2010). In addition, NREL LAPs focus on oil palm biomass flexibility. This contrasts with previous biomass characterization methods, where ADF, NDF and acid detergent lignin (ADL) or TAPPI methods are often followed. However, their application only focused on the scope of pulp and paper (Tan et al. 2016). As can be seen in Figure 3, water and ethanol extraction can eliminate most impurities from biomass. Water extraction isolates inorganic materials, sugars, soil and proteins, while ethanol extracts terpenoid, wax, fatty acids, phenolic and chlorophyll (Sluiter et al. 2010). This extractive removal ensures that

oil palm biomass are free from impurities and contain only structural carbohydrates and lignin. Removing the extractives is a critical step in ensuring the smooth running of acid hydrolysis (Tan et al. 2016).

Characterization of oil palm biomass can be determined through modern scientific equipment such as high-performance liquid chromatography (HPLC), scanning electron microscope (SEM), X-ray Diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. The use of these tools in determining the physical characteristics of the OPF can be summarized in Table 1. The surface morphology of the lignocellulose can be observed using SEM (Owolabi et al. 2016). FTIR can be used to study interactions between functional groups of chemical compounds and their bonds through infrared rays (Darim et al. 2018). XRD method can measure the crystallinity of lignocellulose components (Dewi et al. 2018; Zakaria et al. 2014).

TABLE 1. Summary of various tools for determining the physical characteristics of the OPF

Tools	Observation	References
HPLC	Main sugars in OPF are glucose (80%) and xylose (20%) with total concentration of 67.5 g/L.	Luthfi et al. 2016
SEM	Cell wall surface of OPF is rough and surrounded by pores, unseparated fibres and stucked together with the pores.	Owolabi et al. 2016; Manaf et al. 2018
XRD	Total crystallinity index of OPF is between 45-58%.	Zakaria et al. 2014; Dewi et al. 2018
TGA	Wight of OPF loses considerably at 290°C signifies hemicellulose degradation and at 345°C signifies cellulose degradation.	Owolabi et al. 2016
FTIR	OPF has stretching vibration group (-OH) due to hydrogen bond, (-C-H) due to amorphous phase, stretching (-C-O-C) asymmetric that combines cellulosic oxygen stretching and group (-C-H ₂) known as cellulose crytallinity band.	Darim et al. 2018

PRE-TREATMENT AND ENZYMATIC HYDROLYSIS OF LIGNOCELLULOSIC MATERIALS

The transformation of lignocellulose material into value-added products such as sugar, xylooligosaccharide and lactic acid require necessary pre-treatment steps to make the process more economical. Figure 4 shows the bioprocessing of lignocellulosic biomass into bioproducts. Pre-treatment

is a cost-effective operation, accounting for about 20% of the total processing cost (Bensah & Mensah, 2013). Consequently, the net separation of biomass components through environmentally friendly and economical methods without compromising product quality has been stated by the US Department of Energy as a plausible challenge in the bioprocess industry (Hoekman 2009).

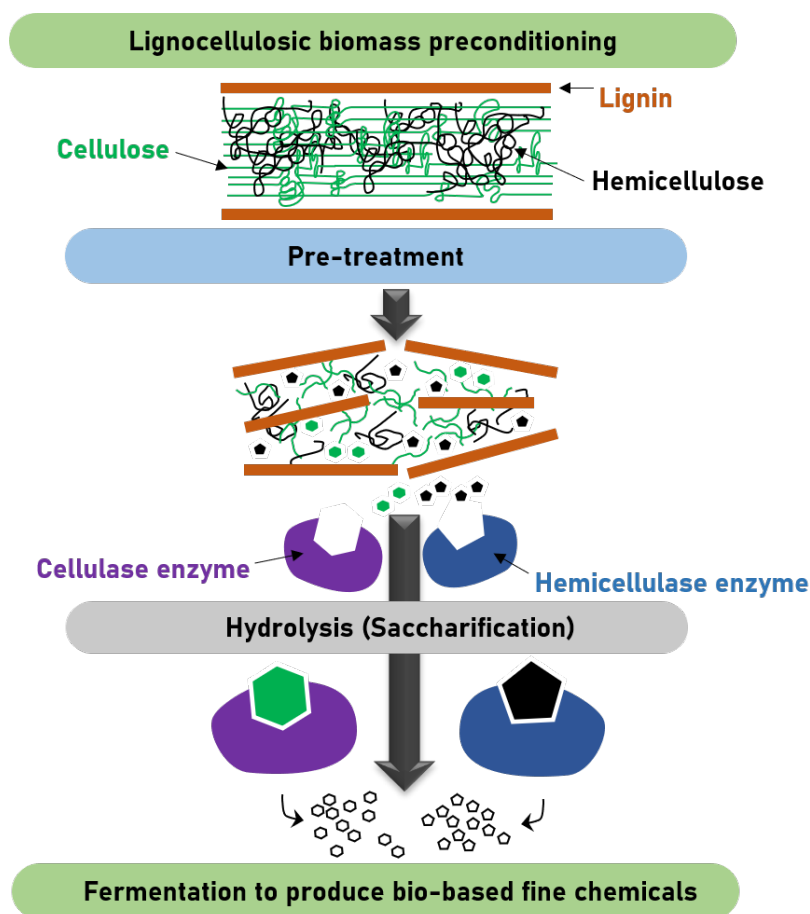


FIGURE 4. Bioprocessing of lignocellulosic biomass into bioproduct

Biochemical conversion of lignocellulose to lactic acid involves two main processes: structural carbohydrate hydrolysis and sugar fermentation to produce lactic acid (Zheng et al. 2010). Hydrolysis catalyzed by enzymes (cellulase or hemicellulase) is considered an environmentally friendly process (Pennacchio et al. 2018). Most lignocellulolytic enzyme producers reported to date are fungi, such as *Trichoderma reesei* (Bischof et al. 2016), *Neurospora crassa* (Dogaris et al. 2013), *Penicillium oxalicum* (Li et al. 2007), and *Aspergillus niger* (Stricker et al. 2008), and bacteria, including *Clostridium acetobutylicum* (Doi & Kosugi, 2004), *Clostridium thermocellum* (Olson et al. 2015), *Bacillus halodurans*

(Annamalai et al. 2013), *Acidotherrnus cellulolyticus* (Wang et al. 2015), *Paenibacillus* sp. (Kanchanadumkerng et al. 2017), and *Bacillus licheniformis* (Marco et al. 2017). Three groups of enzymes that play a vital role in the conversion of cellulose to simple sugars include (i) endo-1,4- β -glucanase to separate glycoside bonds within cellulose; (ii) exo-1,4- β -glucanase or cellobiohydrolase that attacks the reducing end or non-reducing end of the cellulose, thereby forming cellobiose and some cyclodextrins and (iii) β -glucosidase in hydrolysis cellulose and cyclodextrin into glucose. The three groups of enzymes act synergistically to liberate cellobiose and cyclodextrin, which are then converted into monomers (Ioelovich, 2016).

Enzymatic hydrolysis offers advantages such as low energy consumption, little to no side products, and higher sugar yields than acid hydrolysis (Bensah & Mensah, 2013; Canilha et al. 2012). The biotechnology industry has successfully produced enzymes at high protein concentrations and enhanced enzyme activity with significant cost savings in recent developments. Accordingly, the durability of the enzyme and the preservation of hydrolysis operations depends on the value of enzyme activity (Dowe & McMillan, 2001). The production of hydrolytic enzymes is now dominated by two major companies, namely Novozymes (Bagsvaerd, Denmark) and DuPont/Genencor (Danisco, USA), with 47% and 21% market share, respectively (Rodrigues et al. 2015). Several widely used industrial enzymes include Accellerase-1500 and GC-220 from DuPont company. While Celluclast 1.5L, Cellic CTec2 and Cellic CTec3 are produced by Novozymes company in collaboration with Sigma-Aldrich/Merck, which helps expand product marketing networks (Ioelovich, 2016). Hydrolysis using the enzyme is usually carried out at temperatures of 45-50 °C, pH 4.5-5.0 and enzyme loading about 10-20 FPU per gram of substrate (Ioelovich, 2016; Zhu et al. 2008). According to Elzawawy et al. (2011), enzymatic hydrolysis can reduce utility costs as they are operated under mild conditions and are not exposed to erosion problems of operating equipment. Rodrigues et al. (2015) report that recycling Celluclast and Cellic CTec2 enzymes can be done with alkali washing.

The commercialization of commodities from lignocellulose material has a relatively narrow profit margin at present. The use of low solid loading (i.e. less than 5% solid, w/w) provides benefits for research purposes. However, more efficient catalysts lead to new studies using high solid loading to increase industry profits (Bensah & Mensah, 2013). The term “solid loading” refers to the ratio of the quantity of dry matter entering a process to the total amount of mass of a substance and water added (Modenbach & Nokes, 2012). Acid hydrolysis generally depends on the operating temperature and the pK_a value. The concentration of hydrogen ions can be directly linked to the hydrolysis reaction constant; the more negative the value of acid pK_a , the more efficient the saccharification process (Bensah & Mensah, 2013). However, high acid concentrations make the process economically unjustifiable because acid recycling requires high handling and maintenance costs (Elzawawy et al. 2011).

In addition, several factors are identified to affect biomass saccharification. These include material porosity (accessible surface area), cellulose crystallinity, and the content of lignin and hemicellulose (Rodrigues et al. 2015). According to Jonsson & Martin (2016), the presence of

lignin and hemicellulose polymers complicates the enzyme's accessibility to cellulose, thereby reducing the efficiency of hydrolysis. Therefore, pre-treatment steps are needed to alter the structure and morphology of biomass before hydrolysis is carried out. There is a variation in the suitability of a pre-treatment method for different biomass in terms of maturity, harvesting, drying and storage conditions (Ben et al. 2016). Table 2 outlines pre-treatment and hydrolysis with enzymes/acid on various types of biomass in the production of lactic acid.

The selection of an ideal pretreatment strategy depends on the physical properties and biomass composition. Therefore, in order to achieve the effective pretreatment process, the requirements to be met are: (i) improving the fibre reactivity and the ability to be hydrolyzed under high biomass loading; (ii) eliminate certain carbohydrates; (iii) avoiding the formation of by-products that inhibit hydrolysis and fermentation and (iv) are capable of cost-effective processes through energy reduction (Bensah & Mensah, 2013). Biomass pretreatment involves physical processes (such as reduction in size), chemical processes (such as acids, alkalis, salts, oxidizers and solvents), physico-chemicals (such as hydrothermal and ammonium fibre explosions), biological methods (such as white or brown fungus) or a combination of some of these pretreatments to treat the structure of the whole lignocellulose component (Bensah & Mensah, 2013; Chen et al. 2011).

Pretreatment measures are needed to help ensure the biomass is fully utilized. The absence of pretreatment can affect the conversion of sugar and the yield of lactic acid (Corona-Gonzalez et al. 2016). As can be seen in Table 3, all studies of lactic acid that include the use of acids resulted in lactic acid production decreased to less than 50 g/L (Jiang et al. 2016; Aulitto et al. 2017; Nagarajan et al. 2020; Lin et al. 2020; Costa et al. 2020). Although high sugar conversion can be achieved from acid hydrolysis, the formation of inevitable side products can affect the performance of the fermentation process (Elzawawy et al. 2011).

Pre-treatment with acids is often associated with the formation of aliphatic carboxylic acids, acetic acid, formic acid, levulinic acid, phenolic compounds, furfural and 5-hydroxymethylfurfural (HMF) from the degradation of lignocellulose material and its monomers. Aromatic carboxylic acids include phenolic aromatic acids (such as ferulic acid and 4-hydroxybenzoic acid) and non-phenolic aromatic acids (such as cinnamic acid) (Ximenes et al. 2011). Previous studies have reported that soluble phenolic aromatic compounds can affect saccharification performance (Ximenes et al. 2011). The inhibition effect can be reduced by adding oxidant sulfur, such as sulphite

TABLE 2. Pre-treatment and hydrolysis with enzymes/acid on various types of biomass in the production of lactic acid

Substrate	Types of pretreatment	Type of hydrolysis	Microbe	Fermentation process	Lactic acid			References
					Concentration (g/L)	Yield (g/g)	Productivity (g/L/h)	
Wheat Straw	Sulfuric acid-catalysed hydrolysis and steam explosion	NA	<i>Bacillus coagulans</i> , MA-13	Batch	32.05	0.92	2.55	(Aulitto et al. 2020)
Carob	NA	mixture of Accellerase BG and Cellic CTec2	<i>Bacillus coagulans</i>	Batch	48.7	0.84	2.30	(Azaizeh et al. 2020)
Macroalgal biomass	acid/thermal hydrolysis		<i>L. plantarum</i>	Batch	36.8	0.91	7.39	(Nagarajan et al. 2020)
Algal biomass	NA	cellulases and β -glucosidase	<i>Bacillus coagulans</i> Azu-10	Batch	102.2	1.0	3.18	(Abdel-Rahman et al. 2021)
Corn stover	Steam explosion	Cellulase	<i>B. licheniformis</i> RH15	Fed-batch	99.3	0.946	2.48	(Li et al. 2017)
Marine algae	Dilute hydrochloric acid	Cellulase	<i>Lactobacillus (Lb.) acidophilus</i> BCRC 10695	Fed-batch	19.32	0.19	0.268	(Lin et al. 2020)
Ricotta cheese whey	Acid hydrolysis	NA	<i>Lactobacillus casei</i> DSM 20011	Batch	43	0.536	1.05	(Costa et al. 2020)
Corn stover hydrolysate	Acid hydrolysis	NA	<i>B. coagulans</i> GKN316	Fed-batch	45.39	0.83	0.4725	(Jiang et al. 2016)
Glucose	NA	NA	<i>A. succinogenes</i> I30Z	Fed-batch aerobic-anaerobicDual phase	135.6 \pm 0.14	0.96 \pm 0.09	2.94 \pm 0.03	(Li et al. 2010)

TABLE 3. Advantages and disadvantages of various available pre-treatment and hydrolysis for oil palm biomass

Pretreatment/ hydrolysis	Sugar yield	Inhibitor formation	Recyclability	Fermentable sugar	Fermentation yield	Advantages	Disadvantages
Mechanical	L	None	No	No	NA	Breaks down crystallinity of cellulose and increases surface area	High energy consumption
Acid	H	H	Yes	Yes	H	Hydrolysis of hemicellulose, altering lignin structure	Toxic, corrosive and rusty
Steam explosion	H	H	NA	Yes	L	Hemicellulose removal, altering lignin structure	Incomplete disruption of lignin-carbohydrate matrix
Alkali	H	L	Yes	Yes	H	Removal of lignin and hemicellulose, increases enzyme access to cellulose	Long residence time, conversion of alkali to salt remains
Ionic liquid	H/L	L	Yes	NA	NA	Cellulose saccharification, thermally stable, very low vapor pressure	Less effective for hemicellulose and lignin
Hydrothermal	H	L	No	Yes	H	Hydrolysis of hemicellulose, increases enzyme access to cellulose and does not require harmful chemicals	Long residence time, lignin removal is minimal without additional pre-treatment
Enzymes	H	L	No	Yes	H	Non-toxic, mild process and more selective hydrolysis	Requires pre-treatment, sensitive and easily denatured

H: high, L: low, NA: not available.

and dithionite, which react with most aromatic compounds (Cavka & Jönsson, 2013). In addition, sodium borohydride can detoxify the culture medium (Cavka & Jönsson, 2013). In a study by Hong et al. (2012), OPF hydrolysis fractions with sulfuric acid produce very low fermentable sugar due to the severity of the process and the breakdown of xylose to furfural at high concentrations (Hong et al. 2012). Therefore, it is desirable to minimize the formation of inhibitors through the addition of detoxification processes such as activated carbon treatment (Lee et al. 2011) and calcium hydroxide (Jonsson et al. 2013). Acid pre-treatment requires corrosive-resistant materials and less economical treatment units (Jonsson et al. 2013; Wang et al. 2011).

Meanwhile, pre-treatment with water at high temperatures or pressure only forms acetic acid and furan aldehydes due to inadequate hydrolysis. The method is able to dissolve hemicellulose without the need for chemical catalysts (Goh et al. 2010). Table 3 shows the advantages and disadvantages of various types of pre-treatment or hydrolysis available for OPF. Different pre-treatment or hydrolysis methods have different effects on the physico-chemical structure of OPF and the fermentation yield (Menon & Rao, 2012). For example, hydrothermal treatment is expected to achieve a satisfactory fermentation result, in parallel with a small inhibitor formation. Pre-treatment with ionic liquids such as 1-butyl-3-methyl imidazolium chloride ([BMIM]Cl) and 1-ethyl-3-methyl imidazolium-acetate ([EMIM]OAc) is an environmentally friendly method that can dissolve the specific components of OPF. However, some of the ionic liquids are toxic, expensive, difficult to synthesize, moisture sensitive, challenging and time-consuming (Azmi et al. 2018, Smuga-Kogut et al. 2021).

Alkaline pre-treatment, on the other hand, can cause swelling of the biomass and removes phenolic compounds, acetic acid, hydroxy acids, dicarboxylic acids, and hemicellulose in black liquor. Among the various pre-treatment methods available, alkaline pre-treatment using sodium, potassium, calcium, and ammonium hydroxide is considered the best option to reduce the risk of inhibitory formation that would affect fermentative performance (Hong et al. 2012; Hussin et al. 2014).

CONCLUSION

The bio-production of lactic acid from lignocellulose materials such as OPF can benefit various sectors, thereby stimulating economic growth and ultimately offset the socio-economic gap of local communities. OPF is the residue of the palm industry which contributes to the considerable amount of solid agro-industrial waste in Malaysia. Lignocellulose waste management system can be carried out more effectively to improve the saccharification and fermentation processes for conversion to bio-based fine chemicals. Biomass pre-treatment steps are critical to measuring product marketability. In this case, pre-treatment technologies capable of minimizing the number of

inhibitors are indispensable to ensure the smooth operation of hydrolysis and fermentation. The hydrolysis process can be done by enzyme or acid. Enzymatic hydrolysis is a more environmentally friendly method, and its effectiveness depends on the pre-treatment step. Conversely, acid hydrolysis has been widely used in the biomass industry. The detoxification process is needed to prevent the inhibitory effect on cell growth and lactic acid production.

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DECLARATION OF COMPETING INTEREST

None

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