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OVERVIEW OF POLY(LACTIC ACID) PRODUCTION WITH OIL PALM BIOMASS AS POTENTIAL FEEDSTOCK

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ABSTRACT

Poly(lactic acid)(PLA), a bioplastic, is fast gaining attention as the substitute for petroleum derived plastics (petroplastics). However, at present, there is no commercialized PLA production plant that employs oil palm empty fruit bunch (EFB) as feedstock. The main purpose of this paper is to present an overview of PLA production and study the potential of EFB as feedstock to produce PLA. EFB is cheap biomass residue and abundantly available year long in a palm oil producing country like Malaysia. The paper first reviews the market potential of PLA taking into consideration the current developments in bioplastic and petroplastic industries. The paper next discusses the current production technology and highlights the key issues. EFB is proposed as an alternative feedstock for fermentation and its potential is studied from technology and sustainability perspectives. The production process that produces PLA from EFB is outlined with attention to the technological feasibility of the steps. Life cycle analysis and ecoprofile of producing PLA from EFB are presented to showcase its greenhouse gas emissions and fossil energy consumption. It can be concluded that EFB is a highly potential feedstock for commercial PLA production in view of the factors understudied.

Key words: Poly(lactic acid), empty fruit bunch, fermentation, sustainability.

1. OBJECTIVE

This paper presents an overview of PLA production from three perspectives: (i) market potential, (ii) production technology, and (iii) sustainability. For the production technology and sustainability reviews, EFB is proposed as feedstock; and discussion is based on this alternative feedstock.

2. INTRODUCTION

Poly(lactic acid) (PLA) and polyhydroxyalkanoate (PHA) are the most extensively developed bioplastics. Bioplastics are polymers derived from renewable biological sources (biobased) (European Bioplastics, 2014). Common sources are corn, sugarcane, and cellulosic plant materials. Bioplastics are either biodegradable or non−biodegradable. PLA and PHA are bioplastics well known for their biodegradability. Examples of non−biodegradable bioplastics are bio−polyethylene (bio−PE), and bio−poly(ethylene terephthalate) (bio−PET).Bioplastics are believed to have a large market potential as the worldwide plastic market is still experiencing rapid growth.PLA is the bioplastic that garners the most attention as it promises sustainability without compromising the essential properties of established polymers.

PLA is produced by a two step process. First, lactic acid is produced by fermentation and second, the lactic acid monomers are polymerized into PLA. Lactic acid monomer is mostly produced by fermentation of sugar obtained from plant biomass. Oil palm biomass has been studied as feedstock to produce biofuels, which include biomethanol, bioethanol, hydrogen gas, biobriquettes, and pyrolysis oil (Shuit et al, 2009).Empty fruit bunch (EFB), one type of oil palm biomass, is cheap and abundantly available throughout the year in a palm oil producing country like Malaysia. EFB is a lignocellulosic material and it contains 65−80% cellulose and hemicelluloses as rich sugar source. (MohdZainudin et al, 2012). The acid hydrolysis of the cellulose and hemicelluloses yields sugar that is fermented to yield ethanol or methanol. Since bioconversion of EFB into sugar through fermentation has been proven, lactic acid is viable to be produced by utilizing this oil palm biomass. PLA can then be formed by polymerizing lactic acid monomer.

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3. LITERATYRE REVIEW

3.1 Bioplastic Market Potential

In comparison with other bulk commodity materials, plastics are in an early stage of their product life cycle. Figure 1 shows the global production capacity of plastics. The plastics production is estimated to hit 390 million metric tons (MT) in 2050 from 288 million MT in 2012.

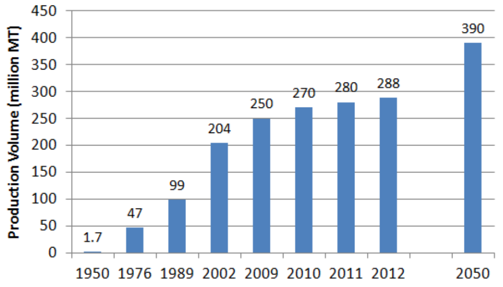

Figure 1: Global plastics production capacity, 1950–2012 (PlasticsEurope, 2013)

According to industry association European Bioplastics (2013a) data as shown in Figure2, the global bioplastic production volume is growing at a compound annual growth rate (CAGR) of 100% from year 2008 to 2010 and forecasted volume for 2015.

As plastic products have shown high demand rate for the past six decades, bioplastics as the substitute for plastics, its market is expected to grow faster than the plastics market with total capacity expected to grow by more than 10% per annum for the next decade. Owing to environmental awareness and fossil oil depletion issues, volume of bioplastics is predicted to increase to around 1,710,000 MT in 2015. The CAGR of bioplatics market between 2009 and 2015 is projected at 32%.

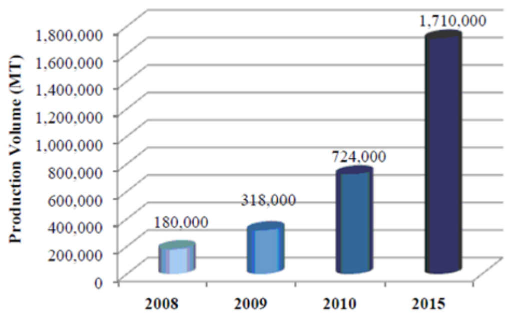

Figure 2: Global bioplastic production volume from 2008 to 2010 and forcasted volume for 2015 (Morgan Stanley, 2012)

Figure 3 shows the global biobased PLA production volume and revenue from year 2007 to 2012. Global PLA production capacity has been on the rise since 2007, hitting a capacity of 200,000 MT in 2012. This production capacity growth is outstanding with a CAGR of 10%. The projected CAGR for year 2014–2020 production is 18.8%.The annual revenue generated grow in accordance to the production volume is from US$135.4 million in 2007 to $439.8 million in 2012. Figure 4 shows that the revenue for year 2020 is forecasted to reach $2,169.6 million.

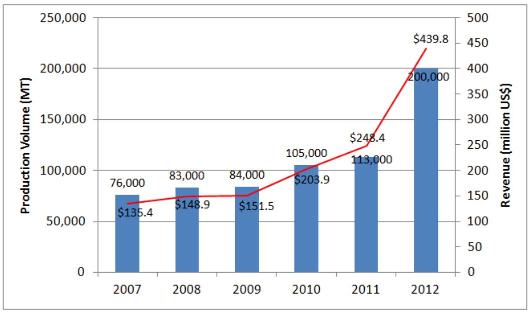

Figure 3: Global biobased PLA production volume and revenue from year 2007 to 2012(SBI Energy, 2012; Grand View Research, 2014)

Based on PLA's economic forecast as shown in Figure 4, PLA revenue is expected to enjoy a steady growth of 15.8% from 2014 to 2020with sales of the biopolymer reaching 800,000 MT in 2020 from 200,000 MT in 2012. Europe and North America are the dominant markets for PLA, whereas Asia Pacific is the fastest growing market. The growth of Asia–Pacific market is expected to be driven by countries like Japan, India, China, and Thailand. This is because countries around Asia Pacific region have cheap availability and wide abundance of raw materials such as sugarcane, sugarbeet, and cassava for lactic acid production. Growing demand for PLA is expected to boost the lactic acid market in the near future. With the demand going strong, existing small scale facilities are set to upscale and commercialize in the future (Widdecke et al, 2010).

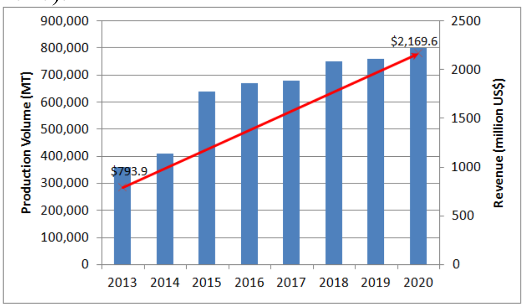

Figure 4: Global PLA market forecast, 2013–2020 (nova Institute, 2013; Grand View Research, 2014)

3.2 Major Industry Players

The leading PLA manufacturer like NatureWorks (USA) has started constructing its second plant in Thailand after having its first facility in USA. The new plant is expected to have a capacity of 140,000 MT/year by 2016 when it starts operation. With this added capacity, NatureWorks will further consolidate its leadership in the global bioplastics manufacturing sector (NatureWorks LLC, 2014).

In late 2011, CSM subsidiary PURAC (The Netherlands) commissioned a 75,000 MT/year PLA monomer plant in Thailand. The raw materials of PURAC's lactide plant are cassava starch and cane sugar, which are locally abundant. CSM expects the bioplastics to gain a broader segment in the plastics market in the future, and the large production of lactic acid presents huge opportunities for industry players (CSM, 2009).

Pyramid Bioplastics located in Germany, a joint venture between Pyramid Technologies Ltd (Switzerland) and German Bioplastics GmbHoperatesa PLA plant using polymerization technology developed by a German company UhdeInventa −Fisher GmbH. The plant commenced operation in the second half of 2009, with a capacity of 60,000 MT/yr(Muhlbauer,2012).

A joint venture between Galactic (Belgium) and Total Petrochemicals (USA) built a pilot plant for manufacturing PLA from sugarbeet and other feedstocks. It is located in Belgium and has a full−fledged operational annual capacity of 1,500 MT. The joint venture company is called Futerro and supported by Total Petrochemicals Research Centre in Feluy, Belgium. (Futerro, n.d.)

3.3 Cost and Price

One major barrier to the widespread usage of PLA is its relatively high price against the petroplastics. NatureWorks LLC prices large volume customers at $2.0 to $2.2/kg ($0.9−$1.0 per pound) in 2012. PURAC's PLA resin is priced at $2.65/kg while Galactic/Total Petrochemicals' PLA is priced at $2.40/kg (ICIS pricing, 2013).The final selling price of PLA product depends primarily on the efficiency of the initial fermentation process to produce the lactic acid monomer. The cost of Lactic acid production currently represents around 40−50% of NatureWorks total cost. PURAC estimated that in its business model, about 50% of the initial investment is required for producing lactic acid, about 30% for lactide and about 20% for the polymer (PURAC, 2009).

3.4 Production Technology

Major PLA bioplastic producers adopt fermentation to produce lactic acid. One of the major hurdles in large scale production is the cost of the raw materials, which accounts for 40% of the production cost in a starch−based facility (Castillo Martinez et al, 2013). The types of raw materials suitable for lactic acid fermentation are sugars, molasses, sugarbeet juice, and whey as well as rice, wheat and potato starches. All materials that contain pentoses (5 carbon sugar) and/or hexoses (6 carbon sugars such as glucose) or materials that can be broken down to pentoses and/or hexoses are feasible feedstock (Nguyen et al, 2013). Recently, other cheaper, non−edible feedstocks have been extensively studied as alternative feedstock for fermentation process. One of the potential feedstocks is lignocellulosic biomass, which looks promising to reduce the cost of PLA in the future (Hagen, 2009). However, a critical bottleneck in the cost is the availability of low cost enzymes to convert cellulose and lignocelluloses into fermentable sugars. It is expected that the cost of these enzymes will be lowered as a consequence of large scale cellulosic ethanol production for application as biofuel.

Lactic acid can be produced by either chemical synthesis ormicrobial fermentation. Chemical synthesis tends to results in racemic mixture of L− and D− lactic acid. Microbial fermentation process is favored by industry players. Fermentation enables the specific production of either L(+) or D(−) lactic acid by using appropriate lactobacillus (Shen et al, 2010). In addition, fermentation offers the advantages of utilizing renewable biomass feedstock, low production temperature, low energy consumption, and the production of highly purified lactic acid by selecting appropriate strain (Abdel−Rahman et al, 2013).

3.5 PLA Applications

PLA has a wide range applications such as packaging (cups, bottles, films and trays), textiles(shirts, furniture),nonwovens(diapers), electronics (mobile phone casing), automotive parts(bumper, dashboard), and cutlery (Sulzer, 2012). At present, NatureWorks' PLA is mainly used in packaging and the textile sector, whereas PURAC is focusing on textiles, buildings and transportation sector. By virtue of its strong mechanical properties, it has been successfully used for medical implants and is approved by regulatory agencies (Lasprilla et al, 2012). Packaging is the largest application market for PLA, accounting for about 60% of the overall market in 2010 (Byun & Kim, 2014). The application areas are expected to be widening due to continual im-

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provements in PLA product properties (Peelman et al, 2013). The more recent development of heat resistant PLA will extend the biopolymer applications to heat resistant textiles and hot drinks cup.PLA blends(Xia et al, 2014; Gallego et al, 2014; Mekonnen et al, 2013) and nano-composite products(Iturrondobeitia et al, 2014; Li et al, 2012; Zhao et al, 2012) have also received increasing attention. The present major hurdle inhibiting the growth of the market is supply limitations and price of PLA, which is higher than oil based polymers (European Bio-plastics, 2013b).

PLA can be the substitutes for low density polyethylene (LDPE), high density polyethylene(HDPE), polypropylene (PP), polyamide (PA), poly(ethylene terepthalate) (PET) as well as seeing possibilities for substituting poly(methyl methacrylate) and polyurethane. PLA is favorable as compared with HDPE and LDPE in terms of its aroma barrier and grease resistance. Comparing with PE, PLA is stiffer and has a higher modulus but it is more expensive. In the non-woven sector, PLA fiber can replace PET and PP to some extents. Although PLA does not reach the heat and impact resistance of PET, its heat resistance is still acceptable. Besides, PLA has a low abrasion resistance as compared to PA, thus limiting its substitution possibility. As to crystal clarity, PLA is less transparent than PA. Both PLA and PA have comparable elongation at break (Hamad, 2012; Lim, 2012).

PLA is competing against other bioplastics for market share. The bioplastic production capacity in 2010 is shown in Figure5. Bio−based PE held the largest share percentage at 27%, whereas PLA and starched plastics held about 16% each respectively. More rapid growth is anticipated for PLA because of unceasing advancements in polymerization and crystallization technology (Lopes et al, 2014; Wu et al, 2014; Harrane et al, 2012; Huang et al, 2012); and also because of its relatively low cost as compared to other bioplastics.

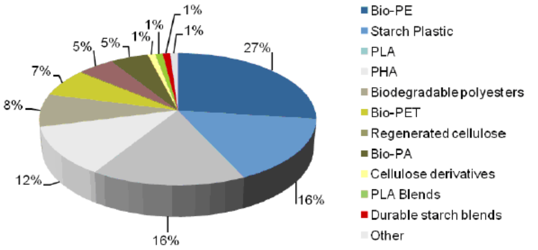

Figure 5: Bioplastics production capacity (%) in 2010(Morgan Stanley, 2012)

Despite the fact that bioplastic is a potential substitute for oil based plastic, the price of bioplastics is still considered high as compared to oil based plastic because of the high-price fermentative production process. As mentioned earlier, the raw materials cost contribute considerably large portion of the total production cost. Cheap raw materials are vital to the development of the bioplastic industry as it could eventually lower the end user cost of PLA. Oil palm empty fruit bunch (EFB) is the potential alternative raw material as fermentation feedstock.

4. DISCUSSION

4.1 EFB Supply

Malaysia is currently the world's second largest producer of crude palm oil. As of 2012, Malaysia hasapproximately5.08 million hectares of oil palm plantation, contributing 39% to the world's total palm oil production and 44% of world palm oil exports. The oil palm industry generates the largest amount of biomass in Malaysia, contributing 85.5% to the total 70 million MT of biomass produced in 2011 (Aljuboori, 2013). Oil palm fronds and trunks are from the tree, while EFB, mesocarpfibre, and palm shell kernel are from the palm oil fruit bunch. 3.4 ton per hectare of EFB is produced annually as biomass (MPOB, 2009a). EFB is normally disposed by incineration, open burning or dumping in landfill. Besides being a potential raw material for PLA, recent studies have revealed that it can be used to produce biofuel and pulp for paper (Tan et al, 2010). Producing PLA from EFB is generating wealth from waste. With such a low cost material, a proposed PLA bioplastic plant using this feedstock will create a large profit margin after recovering the initial investment capital, thereby enhancing the price competitiveness of the PLA against other plastics.

4.2 Technological Feasibility

Oil palm EFB contains up to 80% cellulose and hemicellulose, depending on the source. Table 1 shows the typical composition of EFB. The cellulose and hemicellulose are bound together by lignin, which is hardly accessible by enzyme. Pre-treatment of the lignocellulosic mass is necessary to break down the lignin and to enhance the enzymatic digestibility of the mass during subsequent enzymatic hydrolysis (Li and Kim, 2011).This enzymatic hydrolysis is also known as saccharification.

Table 1: Major components of oil palm EFB (on dry basis) (Mohd Zainuddin et al, 2012)

Components	Content	Typical value
Cellulose	45−50%	48.0%

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Hemicellulose	20−30%	27.0%
Lignin	10−20%	14.5%
Extractive	0−5%	4.0%
Ash	5−10%	6.5%

Owing to its lignin content, EFB has to undergo pre-treatment different to those administered to established feedstocks such as corn and sugar-cane. First of all, the raw EFB is shredded to small particles and dried. In the subsequent pre-treatment, the EFB is treated with acid and/or alkali and undergone delignification for lignin removal (Jeon et al, 2014). It is noted from Table 2 that the ammonia pre-treated EFB has ca. 80% of cellulose and hemicellulose, which are precursors to fermentable sugars. After pre-treatment, the cellulose and hemicellose are well exposed to enzymatic hydrolysis, which will convert the cellulose and hemicellulose to fermentable sugars. These sugars are subsequently fermented into lactic acid.

In an effort to produce bioethanol, various pretreatment methods have been carried out to improve the fermentable sugar yield from EFB (Jung et al, 2011; Kim and Kim, 2013; Cui et al, 2014; Siti Aisyah, 2014). Cui et al (2014) had a 99% of cellulose digestibility after pre-treating EFB with sequential formic acid/calcium hydroxide treatment. Kim and Kim (2013) applied sequential sulfuric acid/sodium hydroxide and obtained over 90% cellulose for hydrolysis. Using a combination of acid and alkali treatment seems to give better result. Jung et al (2011) and Siti Aisyah et al (2014) respectively used aqueous ammonia and sodium hydroxide/CaO, but the cellulose digestibility obtained is less than 50%.

Current technology tends to perform enzymatic hydrolysis and fermentation in a single process unit. This is known as simultaneous saccharification and fermentation (SSF). SSF has a few advantages over separate hydrolysis and fermentation (SHF), such as reduced process time, cost and higher lactic acid yield (Nikolic, 2009). The temperature and pH for optimized yield depend on the strain(s) and enzyme(s) used (Nguyen et al, 2013). Based on Cui et al (2011) and Abdel Rahman et al (2013), the lactic acid yield from EFB using a mixed culture of Lb. rhamnosus and Lb. brevis in batch fermentation can be estimated at 0.70g/g EFB substrate.

The resulting broth from the fermentation process comprises mainly of lactate and counter ions from the base (added to maintain pH), enzymes, impurities from raw materials or fermentation byproducts, residual sugars and polysaccharides, and the microorganisms themselves. In the case of ammonium hydroxide as the base, ammonium lactate will be produced in the fermentation. There are several methods to obtain pure lactic acid from the ammonium lactate salt, namely esterification/saponification, crystallization, lactic acid distillation and extraction (Auras et al, 2010). Other than fermentation, the recovery and purification is also a key step that determines the process economy.

Table 2: Composition of raw and pre-treated EFB (Jung et al, 2011)

components	Raw EFB		After Pre-treatment (with 20% ammonia solution)	
	Mass (kg)	Percentage (%)	Mass (kg)	Percentage (%)
Moisture	60	60	4.452	13.80
Cellulose	19.2	19.2	16.17	50.14
Hemicellulose	10.8	10.8	9.20	28.51
Lignin	5.8	5.8	2.435	7.55
Others(extractive and ash)	4.2	4.2	0.00	0.00
Total	100	100	32.26	100

The polymerization process that produces PLA from lactic acid is nearly the same for most of the commercialized PLA plants. The main differences between commercial facilities are the feedstock used, fermentation conditions, and lactic acid recovery and purification methods.

Once the free lactic acid is obtained, it is sent to a pre-polymerization reactor, where additional water is removed causing the lactic acid to polymerize. The PLA formed in this step is an oligomer of low molecular weight (ca.5000) and therefore not suitable for consumer goods applications. Hence, the PLA is mixed with tin (II) octoate catalyst and sent to lactide reactor. As heat is added, the PLA reacts with the initiating tin (II) octoate catalyst to form lactide, which is a dimer of lactic acid in cyclic structure.PLA of high molecular weight is most commonly produced by ring opening polymerization of lactide (Gruber and Obrien, 2005; Lopes et al, 2014)

The purified lactide proceeds to polymerization reactor to form polylactide which is also known as PLA. Lastly, the resulting PLA is sent to a devolitilizer for purification and then a crys-

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tallizer to form PLA pellets. This PLA is of high molecular weight (ca. 66000) with desired crystallinity for end product applications (Henton et al, 2005).

It is clear that producing PLA from EFB is technologically viable. However, pre-treating EFB is different to pre-treating corn and sugarcane due to its lignin content. This pretreatment is considered the limiting part of the process in terms of production economics. Process integration and optimization are important factors as well that affect process economics. The PLA production is synergizing with bioethanol production in tapping into EFB feedstock. The possible escalation of conventional feedstock price is looming due to food security and other issues. This is certain to add economical advantage to bringing PLA production to scale in the future.

4.3 Substainability

4.3.1 Life cycle analysis (LCA)

The sustainability of converting EFB to PLA needs to be assessed before the proposed PLA plant is set up. LCA is a powerful sustainability measuring tool that provides a thorough analysis of a subject's impact on the environment throughout its entire life cycle. Life cycle assessment for PLA from EFB is conducted to evaluate the environmental impact of the proposed process. Figure 6shows the life cycle of PLA.

Life cycle of PLA is a closed loop from cradle to cradle. At the end of life, PLA- made goods can be composted in a controlled compost environment where PLA might take 45−60 days to break down, under microbial action, into its monomer lactic acid and eventually into carbon dioxide and water plus some humus. These degradation products are absorbed by the growing oil palm trees (Groot and Boren, 2010). Alternatively, PLA can be chemically recycled. It can be converted back to lactic acid and reused for the polymerization process (Vuurens, 2012).

4.3.2 Ecoprofile for PLA

Ecoprofiles are similar to LCA, the difference being the former is a cradle to gate analysis while the latter is a cradle to grave analysis. Ecoprofile, in the case of PLA from EFB, begins with EFB and ends with PLA resins ready for shipment. Ecoprofiles provide a total energy used, raw materials used, gaseous and liquid emissions, and solid waste produced from cradle to gate.

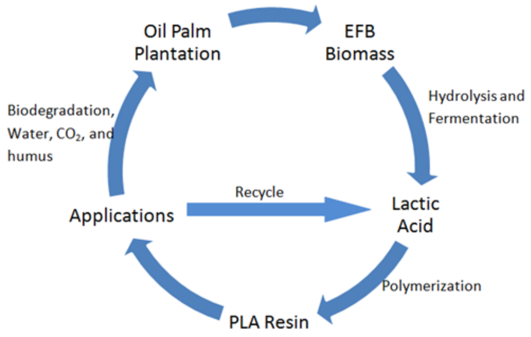

Figure 6: Life cycle of PLA from EFB

Figure 7 shows the ecoprofile of PLA from EFB. One of the attractive features of bioplastics such as PLA is the possibility of carbon neutrality. Carbon neutrality refers to 'net zero' carbon dioxide emission. It results from the uptake of carbon dioxide (CO_2) during photosynthesis of oil palm trees in an amount equivalent to the carbon dioxide (CO_2) emitted during degradation (Vink et al, 2007). Thus, the net zero emission of CO_2 is attained.

However, carbon neutrality is considered as the ideal case and is only true if the processes involved in converting EFB to PLA do not involve any CO_2, which is practically impossible. Nonetheless, the net CO_2 emission for PLA from EFB is bound to be less than that for plastic made from fossil fuel. By adopting current technology and energy use practices, PLA is on par with petroleum based polymers such as PE and PET in terms of utility and has the upper hand on carbon footprint related issues (Vink et al, 2007). This claim is substantiated from the results shown in Figure 8, Figure 9, Figure10, and Figure 11 respectively.

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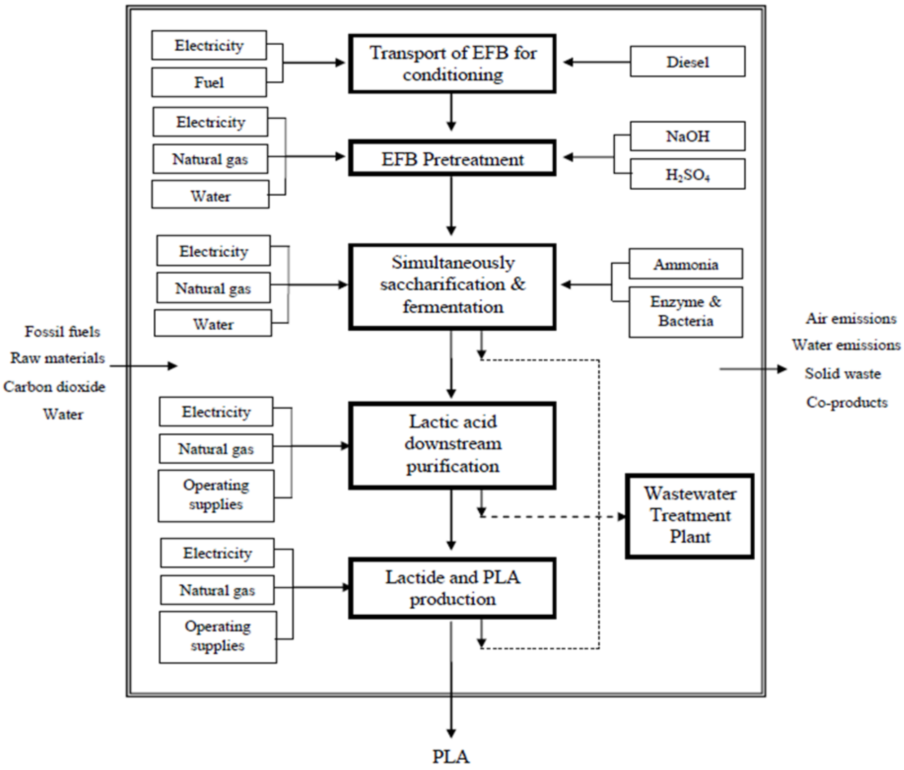

Figure 7: Ecoprofile of PLA from EFB (Vink et al, 2010)

Figure 8 shows that PLA consumes roughly 20 GJ of fossil fuel less than PET does, per ton of plastic produced. As shown in Figure 9, Nature-Works LLC presented similar findings wherein PLA's total energy usage index is lower than PET's by factor of 0.4and the greenhouse gas generation index of PLA is half of PET's as well (Vink et al, 2007).

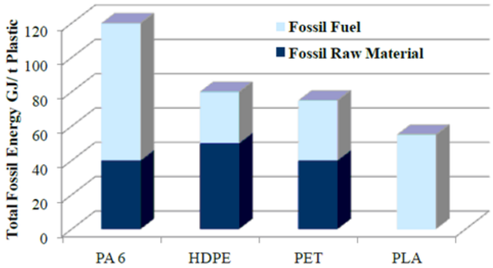

Figure 8: Consumption of fossil resources by PLA vs polymers from fossil feedstock – cradle to gate (PURAC, 2013).

Table 3: Fossil energy usage and greenhouse gas (CO_2 equivalents) generation of PLA and PET (PURAC, 2013)

	PLA	PET
Total Energy Usage Index	1.0	1.4
Percent from renewable resources	56%	<1%
Greenhouse gas generation index	1.0	2.0

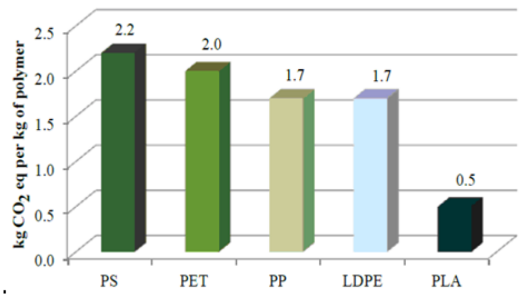

Figure 9: Sustainability on carbon footprint CO_2–cradle to gate (PURAC, 2013).

Table 3 shows that PLA emits much less CO_2 as compared to PS (polystyrene), PET, PP, and LDPE. Comparing with other bioplastics, PLA also requires much less sugar source as raw material. Figure 10 shows that the amount sugar required to produce 1kg of bio–PET is able to produce 3kg of PLA. The amount required for producing 1kg bio–PE is able to produce 2.5kg PLA. Furthermore, PLA has the advantage of being biodegradable over bio–PE and bio–PET which are non–biodegradable.

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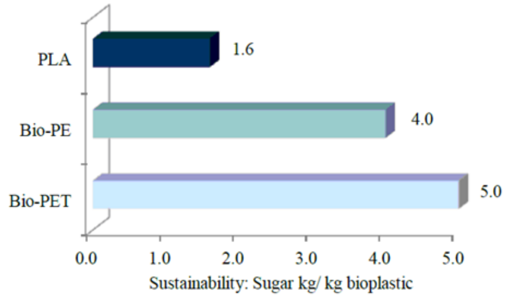

Figure 10: Required fermentable sugar for the production of biopolymers −cradle to gate (PURAC, 2013)

Figure 11 and Figure 12 show the system boundaries for PLA production from corn starch and from EFB respectively. The lignin−rich fraction from the EFB is combustible to provide thermal energy for various conversion processes. Using EFB as raw materials requires less fuel energy input and generates less emission. In a nutshell, choosing EFB has a fourfold advantages, which are no food−fuel supply dispute, less EFB waste disposal problem, less fossil fuel energy consumption, and reduced emissions. All these contribute favorably to the global mega trend−sustainability. It is undeniable that PLA from EFB biomass has great sustainability potential.

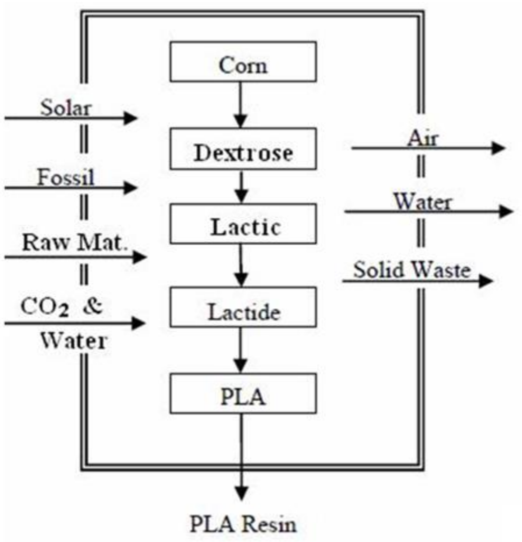

Figure 11: System boundaries for PLA production from corn starch (Vink et al, 2003)

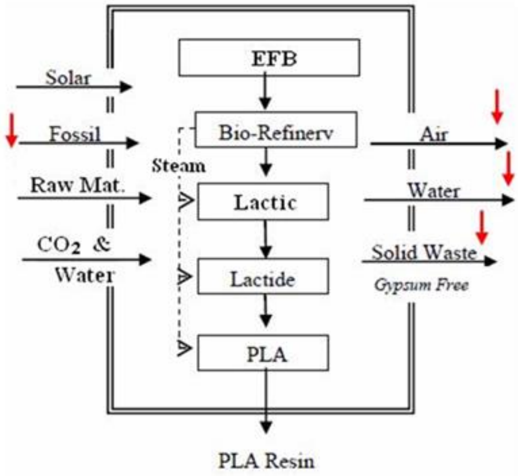

Figure 12: System boundaries for PLA production from EFB

5. Conclusion

Market demand for PLA and its production capacity are forecasted to surge during the 2013−2020 period. Commercial production adopts fermentative process to produce lactic acid using corn starch or sugarcane as feedstock. In view of the high feedstock cost, EFB is highly potential and herein proposed as alternative feedstock in view of the three factors understudied. EFB is cheap biomass waste, abundantly available throughout the year in any palm oil producing country. EFB contains rich amounts of cellulose and hemicellulose as sugar source for microbial fermentation. EFB needs alkaline pretreatment to remove lignin prior to enzymatic hydrolysis. Fermentation−wise, SSF is preferred over SHF due to reduced process cost and time and higher lactic acid yield. As to sustainability, LCA and ecoprofile are presented. Producing PLA from EFB is found to generate less CO_2 than other petroleum based plastics.

Producing PLA requires less sugar than bio−PE and bio−PET. Judging from market, technology, and sustainability points of view, it is concluded that EFB has great potential to be utilized as feedstock to produce PLA commercially.

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