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Biomass Conversion and Biorefinery https://doi.org/10.1007/s13399-021-01371-7 REVIEW ARTICLE

11**Biodiesel from rice bran lipids: resource assessment and technological review**

11**Alchris Woo Go** 1 &**Kristelle L. Quijote** 2 &**Ramelito C. Agapay** 2,3 &**Yi-Hsu Ju** 1,2,4 &**Artik Elisa Angkawijaya** 1 &**Shella Permatasari Santoso**

5 Received: 13 December 2020 / Revised: 7 February 2021 / Accepted: 9 February 2021 Abstract The biodiesel (BD) industry struggles to compete with petroleum diesel because of its high cost, primarily attributed to the costs of raw material and production. Rice bran (RB) is an oleaginous agro-industrial residue which has been of interest as a feedstock for BD production. Although RB has been found to be a potential resource for various products of commercial interest, its current bulk but limited utilization is either as a source of edible oil or as an ingredient of feeds. A key challenge in processing lipids from rice bran is its significant free fatty acid content but is not necessarily a setback when utilized for biodiesel production. Despite the perceived potential, the sheer number of published researches, and even patented processes, there has been no quantitative assessment of the resource availability, and no commercialized process reported. In this work, a localized resource assessment with biodiesel yield estimates has been conducted to identify priority areas for adapting rice bran for biodiesel production. As leading paddy rice producers, Southern, Eastern, and Southeastern Asian regions were found to have potential in adapting RB as a biodiesel feedstock. Alongside this, detailed technological comparisons were described in this review, from lipid

extraction, reaction systems or schemes, reactants, catalysts, reactor configurations and strategies, to emerging and patented technologies with economical and scalable potential. In addition, opportunities in (RB) processing and related government policies, foreseen impacts on economics, social, and environmental aspects, as well as existing challenges, were identified and discussed for future prospects and developments. Keywords Biodiesel . Lipids . Resource assessment . Rice bran . (Trans)esterification Alchris Woo Go and Kristelle L. Quijote contributed equally to this work. * Alchris Woo Go awgo@mail.ntust.edu.tw 1 Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Keelung Road, 10607, Taipei City, Da'an District, Taipei City, Taiwan 2 Department of Chemical Engineering, National Taiwan University of Science and Technology, Keelung Road, 10607, Taipei City, Da'an District, Taipei City, Taiwan 3 Department of Chemical Engineering, University of San Carlos – Talamaban Campus, Gov. Cuenco Avenue, Nasipit Talamban, 6000 Cebu City, Philippines 4 Taiwan Building Technology Center, National Taiwan University of Science and Technology, Keelung Road, 10607, Taipei City, Da'an District, Taipei City, Taiwan 5 Department of Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia 1 Introduction

1**Rice bran (RB) is an** agro-industrial **residue**

generated dur- ing the processing of paddy rice (PR). It is comprised of the pericarp, aleurone, and germ of a brown rice kernel [1]. Typically, RB constitutes 8 to 10 wt% of the PR (~14 wt% moisture) subjected to milling [2]. The actual composition of rice bran generated in rice mills varies

22**depending on the** variety **of** rice, **cultivation conditions, and the**

milling pro- cess adopted [3]. A characteristic of rice bran that makes it unique when compared to other non-oilseed agro-industrial residues is its significant lipid content. Depending on the milling process, lipids in industrially generated RB could range from 4 to 26 wt% [1, 3]. Strictly, RB contains 15 to 20 wt% lipids, with the germ containing as much as 16 to 39 wt% [3]. However, there are tendencies of actual RB generated in rice mills to be adulterated with husk and endosperm particles lowering the resulting bran's lipid content [1]. Rice bran lipids (RBL), in most cases referred to as rice bran oil (RBO), have found applications in food, nutraceuticals, pharmaceuticals, cosmetics, feed, and fuel [4–6]. The use of RBL in food applications as oil has a long history of over 100 years with origins from Japan [4]. Despite this, it continues to face stability challenges owing to indige- nous lipases in the RB that cause rancidity of the lipids [5]. The practical refining yield of RBL to produce refined RBO is only around 50 to 70 wt% of the RBL [4].

14**This is because of the presence of** relatively **higher** free **fatty**

acid (FFA) content as the lipids become rancid and other impurities (gums, waxes, and unsaponifiable matter) found in the crude RBL, with the triglyceride content only at 81 to 84 wt% at most [7]. This is one of the reasons behind the limited use of refined RBO (primarily triglyceride) when compared to other com- mercialized vegetable oil in food applications [6]. The trade of RBO is generally limited within Asia with Thailand (32.4 Gg) as the reported sole exporter for the year 2017 and japan (24.4 Gg) being the largest importer [8]. Rice bran lipids used to be processed mainly for applica- tions in food. However, owing to the presence of phytosterols, tocopherols, tocotrienols, and oryzanols having good biolog- ical activities beneficial for human health, it is also widely explored for possible use as a component in nutraceuticals, pharmaceuticals, and cosmetics [5, 9, 10]. The active compo- nents are oftentimes recovered as by-products after the refin- ing of crude RBL [6], potentially making their production dependent on the RBO industry. If processes would be fo- cused on the recovery of these high-value products, it would not be practical to leave the bulk components (fatty acids and glycerides) of the RBL unused. Other applications of

RBL are in the feed industry, providing similar benefits when used as food, whether as whole bran, its oil, or component lipids [11]. However, it also faces the same challenges in terms of stability of the lipids or dependency in the RBO industry if component lipids are to be tapped. Documents on RBL processing for different applications date back to the 1960s or earlier, based on documents in Web of Science [12] and Scopus [13]. A summary of the document counts on related documents in the past 30 years is presented in Fig. 1. As could be observed, the number of publications on rice bran lipids in its respective application has been continu- ously increasing. Researches on the utilization of RBL as raw material for biodiesel production were prominent after 2000 (Fig. 1d). The number of documents has quickly caught-up with other applications of RBL. Although the number of doc- uments was not further filtered, and may not be the exact number of related published articles, it is indicative of the interest and the perceived need to pursue research and devel- opment in the processing and conversion of RBL to biodiesel (BD). Although FFA is also of concern in biodiesel produc- tion, it could still be converted into the desired fuel. Depending on the composition of the RBL, BD yield

4**in the form of fatty acid methyl ester (FAME**

) ranges from 85 to 93 kg per 100 kg of RBL [14–16], which is higher than refin- ing of RBL to RBO. Moreover, depending on the process adopted, active components are still recoverable [17]. One of the earliest estimates reported regarding the po- tential amount of BD from RBL was in 2008. Ju and Rayat [18] estimated that top rice producers in Asia could support up to ~10 hm3 (10 million cubic meters, MCM) of BD, which on average displaces 10% of these countries' petro- leum diesel (PD) requirements during that period. However, these estimates may not anymore be true today. Moreover, the details on how the estimates were made and the assumptions behind the estimates are not provided. A more localized estimate was made by Gunawan et al. [19] in 2011 on the potential of RB as a source of biodiesel in Indonesia. It was estimated that ~96 Gg of BD could be generated per year in Indonesia from an annual RB pro- duction of ~3 to 6.5 Tg with a lipid content in the bran of ~14 wt% and a FAME yield of ~50% via in situ transesterification (ISTE). Unfortunately, it is unclear as to how much the estimated potential could contribute to the PD demand in Indonesia and how it would fare in the current context. In 2013, Hasan et al. [20] looked into the prospects of biodiesel from RB in Bangladesh, considering PR production in the years 2008 to 2011. The estimated annual BD from RB between 0.91 and 0.98 Tg (~1.03 to 1.11 hm3) could meet up to 60 to 70% of the PD demand in Bangladesh. One main concern on the estimations made is the assumption that rice bran and husk constitute 20 wt% of the PR and that the combined residue contains 20 wt% lipid. These assumptions easily overestimate the potential BD from RB. Rice bran as a resource for biodiesel produc- tion in India was tackled by Sundar et al. [21] in 2019; however, there was neither clear quantitative basis nor es- timates to support claims on the use of RB as a resource. In the Philippine context, Go et al. [22] provided estimates and projections of RB when used as a resource for biodie- sel spanning from the years 2000 to 2040, and suggested that using RB as the sole resource could support the Philippine BD demand if the blending is to be kept at 2 vol.%. Although assumptions were provided, and relative- ly conservative estimates were made, reevaluation is nec- essary as the actual BD blending greatly depends on changing government policies and mandates. The interest in using RB as a resource for BD produc- tion is mainly hinged on the following ideas: (i) abun- dance, availability, and underutilization of RB in rice- producing countries [19–22]; (ii) limited application in food and related industries due to poor stability of lipids in RB [17, 23]; (iii) poor economic competitiveness of resulting RBO, owing to costly stabilization methods and low refining yield [17]; and (iv) low-cost material com- pared to other resources and recovery of high-value by- the synthesis of BD from RBL and focused on the later et al. [24] in 2021 has made brief discussions related to recent review on BD derived from RBL by Hoang covering developments from 2000 to 2010. The most technologies in RBL extraction and (trans)esterification further included the discussion of supercritical solvent recent book chapter by Zaidel et al. [23] in 2019 has including in situ transesterification of RBL. The most advancements in RBL processing for BD were discussed, and the potential biodiesel that could be produced from determine the world production and distribution of PR & RB, The main objectives of this assessment and review are to (i) lated state-of-the-art advancements in BD production and use. the limitations of the practical utilization of RBL and the re- technologies in BD production from RB, to better understand assessment of resource availability, and detailed review of that these will be addressed through a simple and practical With the gaps observed from available literature, it is hoped was later written by Ju and Rayat [18] in 2008, where developments in converting RBL to DB. A book chapter done by Ju and Vali [17] in 2005, which covers the early different technologies to produce BD from RB has been cess parameters greatly differ. The first review on the cooking oil) resources, although technologies and pro- rapeseed, palm, and coconut) and non-edible (used/waste produced industrially from different edible (soybean, trial scale production. Biodiesel has been successfully an excellent BD resource, it has not proceeded to indus- products [17, 18, 20]. Although these ideas justify RB as version to produce BD in a bio-refinery approach. and RBL components during their processing and con- and different approaches in maximizing the use of RB 2020, which include subcritical solvent technologies RBL did not cover major developments from 2010 to reviews on the technologies for BD production from [5, 9, 11], and its applications [4, 6]. However, past zation [25], extraction [6], refining [7], nutritional value pers on RBL processing mainly focused on RBL stabili- mance of the engine using such fuel. Other review pa- use of the synthesized BD as fuel and related perfor- be printed in black and white. a Food (rice bran oil AND food NOT are not mutually exclusive). *Search term with Boolean operators.—To Scopus [13] databases up to June 2020 (number of documents indexed or oil applications since 1991 as indexed in Web of Science [12] and Fig. 1 An estimate of the number of publications related to rice bran lipid (Rice Bran Oil AND Feed NOT Nutraceutical NOT Pharmaceutical)* (c) Feed 1991 1992 1993 1994 1995 1996 1997 1998 2000 1999 2001 Publication Year 2003 2002 2004 2006 2005 2007 2008 2009 2010 2011 2013 2012 2014 2015 2016 2017 2018 2019 2020 Number of Documents 0 10 20 30 40 50 60 NOT Pharmaceutical NOT Biodiesel)* (Rice Bran Oil AND Food NOT Nutraceutical Web of Science Scopus (a) Food Number of Documents 0 10 20 30 40 50 60 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 Web of Science Scopus Publication Year 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 bran AND biodiesel)* nutraceutical NOT pharmaceutical)*. d Rice bran and biodiesel (rice pharmaceutical OR cosmetic)*. c Feed (rice bran oil AND feed NOT pharmaceuticals, and cosmetics (rice bran oil AND nutraceutical OR nutraceutical NOT pharmaceutical NOT biodiesel)*. b Nutraceuticals, (Rice Bran AND Biodiesel)* (d) Rice Bran and Biodiesel 2000 2001 2002 2006 2003 2004 2005 Publication Year 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 Number of Publications 0 10 20 30 40 50 60 Web of Science Scopus (b) Nutraceuticals, Pharmaceuticals, and Cosmetics (Rice Bran Oil AND Nutraceutical OR Pharmaceutical OR Cosmetic)* Number of Documents 0 10 20 30 40 50 60 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 Web of Science 2001 Publication Year 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 Biomass Conv. Bioref. available resources in prospective regions and countries; (ii) review the technologies and developments in the conversion of RBL to BD from 2000 to 2020 and its use as fuel; (iii) elucidate the main process parameters and responses influenc- ing the conversion of RBL to BD and process assessment, respectively; and (iv) provide a brief overview of the foreseen social, economic, environmental, and government policy im- pacts or implications when utilizing RBL in DB production and its subsequent use. 2 Resource assessment and review methods Statistical data on the

4**production, supply, and** trade **from** 1960 **to 2018 or recent data available for** PR, **diesel, and**

biodiesel, as well as published researches on BD from RBL, were gath- ered from recognized international and government databases and reports. These databases and reports include the

4**United States Department of Agriculture (USDA)—Foreign Agriculture Services (FAS**

) [8, 26], United Nations Data [27],

4**Global Agricultural Information Network (GAIN) Report**

[28], Scopus [13], and Web of Science [12]. 2.1 Estimating potential biodiesel from rice bran Estimating the potential BD (PBD) from rice bran lipids will be done by adopting Eq. (1). The available lipids (MRB × CLipid), with the lipid content (CLipid) taken to be 0.15 w·w−1, are multiplied by the recovery factor (frecovery = 0.95) and process yield (YBD/Lipid),

4**defined as the mass of** BD pro- duced **per mass of the** lipid **processed, to estimate the amount of renewable diesel. The density of the desired renewable diesel** (ρBD) **is then used to convert the available BD in terms of volumetric quantities. In most cases, in the production of FAME BD, the product of**

YBD/Lipid and ρBD−

4**1 is generally taken to be 1** hm3 **BD**

(or 1 MCM) per Tg oil. PBD ¼ M RB CL f recovery Y BD=Lipid ρBD−1 f A f U ð1Þ To estimate the mass of RB (MRB), Eq. (2) is used. Bran fraction (XBran) of available PR (MPR) is taken to be at the minimum of 0.08 w·w−1 with the moisture at 0.14 w·w−1. Milling (fML) and logistic (fLL) fractional losses are taken to be 0.05, while availability (fA) and use (fU) factors were taken to be 1. M RB ¼ M PR X Bran ð1−CM Þ ð1− f MLÞ ð1− f LLÞ f A f U ð2Þ 2.2 Gathering of available literature and scope of review Prominent indexing sites Scopus, Web of Science, and Google Scholar were used in gathering related literature on BD from RB from the years 2000 to 2020. The scope of this review will be limited to and is sectioned according to the following areas: (i) characteristics of RBL, (ii) the potential of BD from RB, (iii) extraction and recovery of RBL, (iv) process options for BD production, (v) variables affecting BD production productivity, (vi) BD from RB as fuel, (vii) foreseen impacts of utilizing RBL as feedstock for BD pro- duction, and (viii) foreseen challenges and research opportunities. 3 Results and discussion As have been mentioned, RB is a by-product during the mill- ing of PR. Therefore, its production volume and availability is greatly dependent on the PR produced and processed. Considering that PR is traded and consumed after milling, local production of PR is indicative of their capacity and po- tential to produce RB. Shown in Figs. 2 and 3 are the PR production in different regions in the world from 1961 to 2018. As could be observed, PR production has generally been increasing in the past 6 decades (Fig. 2a). Compared to the production in 1961 (215.7 Tg), the production in 2018 (782 Tg) is ~3.6 times as much, which on average translates to an annual increase of ~2% (9.8 Tg per year) in the past 6 decades. The production of PR is consistently concentrated in Asia with an annual share of 91.21 ± 0.61%, followed by America (5.15 ± 0.38%) and Africa (2.78 ± 0.68%). Within Asia, PR production is further distributed between Eastern (42.14 ± 5.82%), Southern (32.09 ± 2.33%), and Southeastern (25.57 ± 3.98%) Asia (Fig. 2b). The production of PR within the major sub-regions in Asia is generally increasing over time (Fig. 3a–c), except for the production in Eastern Asia (Fig. 3a) where there is an ob- served slowing down in production rate. Given the area har- vested (Fig. 3d–f), there has been a decline in the harvested area in Eastern Asia (Fig. 3d), while there is a significant increase in the harvested area in Southern Asia (Fig. 3e) and Southeastern Asia (Fig. 3f) from 1961 to 2010. However, in the past 8 to 10 years, it could be observed that the area har- vested in East (3.34 ± 0.04 × 105 km2), South (6.11 ± 0.11 × 105 km2), Southeast (4.88 ± 0.11 × 105 km2) Asia has remained relatively the same. Although there is no significant increase in the harvested area in the past decade, the recorded production in PR still increased. This increase translates to improved yields (Fig. 3g–h) in PR over the year, which may be attributed to improvements in agricultural practice, rice species, and harvesting technology. Among the sub-regions Biomass Conv. Bioref. Fig. 2 World annual paddy rice production by geographic regions from 1961 to 2018 (statistical data obtained from FAOSTAT [26]).—To be printed in black and white. a World paddy rice production. b Paddy rice production in Asia Production (Mt or Tg) 800 700 600 500 400 300 200 100 0 1961 1963 1965 1967 1969 1971 1973 1975 1977 1979 1981 1983 1985 1987 1989 1991 1993 1995 1997 1999 2001 2003 2005 2007 2009 2011 2013 2015 2017 Year Africa Americas Asia Europe Oceania (a) World Paddy Rice Production 800 Production (Mt or Tg) 700 600 500 400 300 200 100 0 1961 1963 1965 1967 1969 1971 1973 1975 1977 1979 1981 1983 1985 1987 1989 1991 1993 1995 1997 1999 2001 2003 2005 2007 2009 2011 2013 2015 2017 Year Central Eastern Southern South Eastern Western (b) Paddy Rice Production in Asia in Asia, yields in Eastern Asia have reached as high as ~0.70 increased hydrolytic activity of indigenous lipase where- kg·m−2, while yields in Southern and Southeastern Asia were by free fatty acid contents could increase from 6 to only at ~0.43 kg·m−2. The prediction of yields and production 14 wt% in the extracted lipids to as much as ~60 wt% of crops like PR is not straight forward as it is influenced by in 2 months [14, 29, 30] and up to 82 wt% after 6 various environmental factors, along with cultivation, and har- months of storage [14, 30]. The available extractable vesting practices. However, the available data is indicative lipids in bran typically range from 14 to 19 wt% [31, that PR yields in Southern and Southeastern Asia could still 32]. Variability in RB's extractable lipids or total lipid be improved. Regardless, having PR production concentrated content is mainly attributed to the variety of PR, and in Eastern, Southern, and Southeastern Asia, the potential milling technique employed [1, 3]. However, the extract- generation and advantageous utilization of RB would be in able lipids also decrease with prolonged storage of RB. countries in these regions. Detailed analysis of its components revealed that the glycerol backbone released after complete hydrolysis of 3.1 Characteristics of rice bran lipids and its derived an acylglyceride (AG) was not anymore extractable by n- FAME biodiesel hexane resulting in a lesser amount of extractable lipids but the total fatty acids (TFA) extractable from RB Milling of PR would require the grains to have a mois- remained the same [14]. Apart from FFAs and AGs, ture content between 13 and 14 wt%, with the grain which comprise ~85 wt%, RBL also contains wax esters, temperature not exceeding 45 °C throughout the process, phospholipids, and unsaponifiable matter. The compo- to achieve the best milling results [2]. Along the milling nents of RBL, excluding the unsaponifiable fraction, process, while the bran fraction (8 to 10 wt% [2]) is could be converted to biodiesel (alkyl esters). For each removed from the grain, the bran fractions are scored 100 g of RBL, there is 81 to 89 g TFA, translating to 85 exposing the indigenous lipases with the storage lipids to 93 g FAME [14–16]. [3]. These milling conditions induce the environment Considering that biodiesel is composed of fatty acid alkyl for the hydrolysis of the lipids even after the milling esters of different fatty acid chain lengths and saturation, BD process. The moisture content of 10 to 20 wt% and stor- properties are greatly influenced by their distribution in the age temperatures between 30 and 50 °C result in the resulting fuel. Presented in Table 1 are distributions of fatty Eastern Asia Southern Asia Southeastern Asia 300 250 Production (Mt or Tg) 200 150 100 50 y = 2.2052x - 4,203.9703 y = 3.2329x - 6,284.9468 y = 3.2975x - 6,439.4619 0 R² = 0.8208 R² = 0.9728 R² = 0.9738 1950 2000 2050 1950 2000 2050 1950 2000 2050 Year Year Year a b c 7.0E+05 6.0E+05 Area Harvested (km2) 5.0E+05 4.0E+05 3.0E+05 2.0E+05 y = -949.9173x + y = 2,462.9112x - y = 3,922.8519x - 1.0E+05 2,246,542.2401 4,337,682.2911 7,419,319.6190 R² = 0.3247 R² = 0.8924 R² = 0.9635 0.0E+00 1950 2000 2050 1950 2000 2050 1950 2000 2050 Year Year Year d e f 1.00 0.90 y = 0.0077x - 14.8536 y = 0.0047x - 9.0221 y = 0.0054x - 10.4705 R² = 0.9428 R² = 0.9702 R² = 0.9906 0.80 Yield (kg/m2) 0.70 0.60 0.50 0.40 0.30 0.20 0.10 0.00 1950 2000 2050 1950 2000 2050 1950 2000 2050 Year Year Year g h i Fig. 3 Trends in annual paddy rice production (

22**a, b, c**), area harvested (**d, e, f**), and yields (**g, h, i**

) in Eastern (a, d, g), Southern (b, e, f), and Southeastern (c, f, i) Asia (Statistical data obtained from FAOSTAT [26]) acids from RBL of different origins expressed as methyl esters and their estimated biodiesel properties. The three main fatty Table 1 Rice bran lipid fatty acid profile and corresponding biodiesel properties Source 1 China Reference [33] 2 3 Taiwan India [30] [34] 4 5 6 7 8 Indonesia Thailand Philippines The U.S. Brazil [35] [36] [37] [38] [39] ASTM D6751 [40] EN 14214

3**Fatty Acid** Profile **Lauric (C12:0) Myristic (C14:0**

)

17**Palmitic (C16:0) Palmitoleic (C16:1) Stearic (C18:0) Oleic (C18:1) Linoleic (C18:2) Linolenic (C18:3**) Arachidic (**C20:0**) Eicosenoic (C20:1) **Behenic (C22:0**

) Lignocergic (C24:0) Biodiesel Properties b 3.3 - 26.5 - 1.0 32.9 31.1 4.7 0.1 0.2 - - 0.2 0.8 17.7 0.2 2.2 40.6 35.6 1.8 0.2 - 0.3 0.6 Saturated Fatty Acids, SFA 30.90 22.00 Monounsaturated FA, MUFA 33.10 40.80 Polyunsaturated FA, PUFA 35.80 37.40 Degree of Unsaturation, DU 104.70 115.60 Iodine Value, IV (g I2 per 100 g) Saponification Value, SV (mg·g-1) 98.95 106.12 206.39 202.92 Cetane Number, CN 50.48 49.32

3**Density (kg·m-3**) 870 870 **Kinematic Viscosity**

(mm2·s) 3.63 3.78 Higher

3**Heating Value (MJ·kg-1) 39**.26 **39**

.54 Long-Chain Saturated Factor 3.25 4.72 Cloud Point, CP (°C) 8.95 4.32 Pour Point, PP (°C) 2.89 -2.13 Cold Filter Plugging Point, CFPP (°C) -6.27 -1.65 Allylic Position Equivalents, APE 104.50 115.40 Bis-Allylic Position Equivalents, BAPE 40.70 39.54 Oxidation Stability Index, OSI (h) 5.88 5.74 OSI by Knothe and Dunn (h)d 2.07 2.13 0.1 0.1 1.0 0.4 15.0 20.9 - 0.3 1.9 2.0 42.5 42.5 39.1 32.2 1.1 1.2 0.5 0.1 - 0.5 0.2 - - - 18.70 23.50 42.50 43.30 40.20 33.40 122.90 110.10 112.05 100.54 205.03 203.56 47.71 50.49 880 870 3.82 3.78 40.01 39.53 3.25 3.19 2.90 6.00 -3.68 -0.31 -6.27 -6.45 122.90 109.30 42.30 34.80 5.52 6.12 2.01 2.34 - - - 0.3 18.3 13.7 - 0.1 2.4 1.6 41.4 35.4 37.9 46.9 - 1.5 - 0.3 - - - 0.2 - - 20.70 16.10 41.40 35.50 37.90 48.40 117.20 132.30 105.88 120.99 202.45 201.76 49.44 46.13 870 870 3.74 3.67 39.46 39.45 3.03 2.77 4.63 2.21 -1.79 -4.42 -6.96 -7.77 117.20 132.20 37.90 50.50 5.70 5.03 2.20 1.64 - - - - 11.2 18.7 - - 2.6 - 32.9 43.4 45.9 37.9 3.1 - 4.3 - - - - - - - 18.10 32.90 49.00 130.90 121.21 200.60 46.24 870 3.74 39.48 6.72 0.90 -5.85 4.64 130.90 60.70 5.00 1.18

5**n.a**.a **n.a. n.a. n.a. n.a**

.

5**n.a. n.a. n.a. n.a. n.a**

.

5**n.a. n.a. n.a. n.a. n.a**

.

5**n.a. n.a. n.a. n.a**. ≤ 12 **n.a**

.

5**n.a. n.a. n.a**. 18.70 **n.a. n.a**

. 43.40

5**n.a. n.a**. 37.90 **n.a. n.a**. 119.20 **n**

.s.c n.s. 107.68 n.s. ≤ 120 202.56 n.s. n.s. 49.02 ≥ 47 ≥ 51 870 n.s. 860 – 890 3.74 1.9 – 6.0 3.5 – 5.0 39.45 n.s. n.s. 1.87 n.a. n.a. 4.84

5**n.s. n.s**. -1.56 **n.s. n.s**. -10.60 **n.s. n.s**

. 119.20

7**n.a. n.a**. 37.90 **n.a. n.a**

. 5.70 ≥ 3 ≥ 6 2.20 ≥ 3 ≥ 6 a n.a. not applicable; b biodiesel properties were estimated using “Biodiesel Analyzer© Ver. 2.2” (available on “http://www.brteam.ir/biodieselanalyzer”) with empirical correlations based on related literature [41, 42]; c n.s. not specified; d estimated using correlation established by Knothe and Dunn [43], where OSI = 3.91–0.045 × BAPE acids found in RBL are palmitic (11.2–26.5 wt%), oleic (32.9–43.4 wt%), and linoleic (31.1–46.9 wt%) acids (Table 1). The presence of behenic and lignoceric acids in RBL samples may be indicative of the presence of husk frac- tions in the collected RB [3]. Collectively, chain

3**length and degree of** unsaturation **of fatty**

acids are expressed as saponification value (SV) and iodine value (IV), respectively. The SV of FAME from RBL is between 200 and 206 mg·g−1 because it consists largely of long-chain fatty acids with lauric acid (280 mg·g−1) as the shortest fatty acid and lignoceric acid (152 mg·g−1) being the longest FA chain in commercial BD. As for the IV, BD de- rived from RBL ranges from 99 to 121 g I2 per 100 g FAME. Fatty acids from RBL are considerably unsaturated but could generally pass limits (≤ 120) stipulated in the European Standards (EN). Both

3**chain length and degree of unsaturation**

influence the

3**quality of the** resulting **biodiesel**. Comparing **the** esti- mated **properties of** potential FAME from RBL to stan- dards outlined by

25**ASTM (American Society for Testing and Materials) and** EN, most of **the**

physicochemical properties have been met when compared to ASTM, but fall short in some properties when compared to EN stan- dards. For instance, the cetane number (CN) could range from 46 to 50, which does not meet current standards by EN and could also fall short in ASTM standards. The CN is strongly correlated with SV and IV, with lower SV and IV resulting in higher CN [44]. This idea could be taken advantage of by blending with FAME derived from lipids of longer chain lengths and higher saturation to improve the CN of BD from RBL. However, actual tests of FAME from RBL following ASTM D 613 resulted in CN ranging from 48 to 61 [45–47]. Although no strict standards are set for cold flow properties, FAME from RBL have fa- vorable cold flow properties suitable for use in the tropi- cal (T ≥ 18 °C) and the subtropical (T = −3 to 22 °C) zones, where Southeastern Asian countries and part of Southern and Eastern Asian countries are located. It is also worthwhile noting that the presence of unsaturation improves the cold flow properties of BD, allowing its use in colder conditions [48]. One of the main concerns in the use of BD is its oxidative stability, owing to the high degree of unsaturation. Estimates of oxidative stability index (OSI) for pure FAME from RBL using “Biodiesel Analyzer© Ver. 2.2” ranges from 5 to 6 h, which are estimated using the correlation based on the linoleic and linolenic contents as previously established by Park et al. [49]. However, adopting the correlation established by Knothe and Dunn [43], the estimated OSI only ranged from 1 to 2 h. Studies performing an actual test for oxidative stabil- ity (OS) of FAME from RBL had varied results with 4 studies reporting in the range of 1.61–1.92 h [47, 50–52], 3 studies reporting 3.65–5.00 h [53–55], and one as high as 9 h [56]. These variabilities and discrepancies of estimated and mea- sured oxidative stability index may merit further investiga- tions to provide accurate estimates, and reliable measure- ments, for appropriate evaluation. Nevertheless, the issue on OS could be addressed by adding antioxidants or additives, which is normally practiced for commercialized BD to meet standards [53]. Moreover, natural antioxidants like tocoph- erols, tocotrienol, and oryzanol present in RBL could contrib- ute to improving the OS of resulting FAME [57]. For the use of fatty acid alkyl ester (FAAE) from RBL as BD, whether used neat or in blends with PD and alcohols, an extensive review has been made by Hoang et al. [24] covering different researches that focused

3**on the** engine **performance, combustion, and emission characteristics**

. From the said re- view, it was concluded that a 20% blend of RBL-BD by vol- ume with PD was recommended as it provided similar com- bustion characteristics and engine performance but at reduced emissions as compared to neat PD. With BD from RBL hav- ing potential and practical use in the diesel fuel market, it would be of importance to know the availability of the re- source and the challenges faced in converting the lipids into the desired renewable fuel. 3.2 Potential biodiesel from rice bran lipids One of the main drivers in the use of renewable fuels like that of BD is to reduce dependence on the foreign supply of fuels. Thus, biofuel producers should first ensure the availability of a local resource. In Eastern Asia, 91.04 ± 0.49% of the PR is produced in China, and Japan having a share of 4.58 ± 0.28% in the past decade. For Southern Asia, PR production is main- ly distributed between Bangladesh (22.43 ± 0.65%) and India (68.32 ± 0.94%). As for Southeastern Asia, production is dominated by Indonesia (34.63 ± 2.36%), followed by Vietnam (20.47 ± 0.75%), Thailand (15.84 ± 2.11%), Myanmar (13.15 ± 1.63%), and the Philippines (8.50 ± 0.39%). Interestingly, most of these countries also advocate the use of BD (Fig. 4). From Fig. 4a–c, it could be observed that on-road diesel consumption has continuously increased from 2000 to 2018, except for Japan and Myanmar averaging an annual consumption of ~0.35 and ~0.54 hm3, respectively. In view of BD production and consumption (Fig. 4d–f) from these countries, these have also increased over the years. This is most likely a response to their commitment to the Kyoto Protocol (2005) [18]. For most countries producing BD in Asia, there seems to be a big gap between the production and what is consumed, ex- cept for the Philippines. This indicates that the use of BD may not only be for on-road applications, and that part of what is produced is exported. A closer look into the production, con- sumption, and trade of BD by the countries (Table 2) further reveals that the consumption has since expanded from on-road to other transport and industrial use, except for the Philippines and Malaysia. Moreover, most of these countries expanded their production capacities to a point, which enabled them to export the BD they produced, except for India, the Philippines, and Thailand. For most Asian countries implementing the use of BD, except China and Japan, there is targeted blending percentage of BD into the diesel fuel sold in the market, based on government mandates. Unfortunately, many of these countries are not able to meet their current mandates or are still far from meeting their targets, except Thailand. In the context of Southeastern Asia, a recent review has pointed out that only Malaysia and Indonesia have surplus oils from palm to be used for BD production [58]. From the said review, countries in Southeastern Asia could potentially meet their mandates if surplus oils from palm and coconut are solely used in BD production and trade is limited within the region, having at least an annual potential of ~36 MCM (~36 hm3). The availability of an additional resource would be im- portant in meeting blending targets and minimizing the use of PD, while still allowing the trade of edible oils. Implementing the use of biofuels like BD requires a pool of feedstock to successfully meet demands or realistically dis- place or minimize the use of petroleum-based fuels while avoiding the competition in the use of edible oils [22]. Japan, China, India 150 On-Road Diesel Consumption (hm3) 100 50 0 Japan China India 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 Year Total BD Produced and On-Road Consumed (hm3) 0.05 0.04 0.03 0.02 0.01 0 Potential BD from RB 0.12 0.1 Lipids (hm3) 0.08 0.06 0.04 0.02 0 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 a# 1.2 (Japan – Primary Axis) 1 0.8 0.6 0.4 0.2 0 Year d* (Japan – Primary Axis) 3 2.5 2 1.5 1 0.5 0 30 25 20 15 10 5 0 Malaysia, Indonesia, Thailand Malaysia Indonesia Thailand 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 Year b# 1.4 6 1.2 (Malaysia – Primary Axis) 5 1 0.8 4 0.6 3 0.4 2 0.2 1 0 0 Year e* 0.03 0.025 (Malaysia – Primary Axis) 1 0.8 0.02 0.015 0.6 0.01 0.4 0.005 0.2 0 0 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 Year g Fig. 4 Trends in on-road diesel consumption (a, b, c) [27, 28], biodiesel production and on-road consumption (d, e, f) [28], and potential BD (g, h, i) from rice bran (RB) lipids (estimated from paddy rice production [26], assuming paddy rice with 14 wt% moisture [2], 8 wt% bran [2], and bran Taking Indonesia as an example, even if all the BD produced in 2018 is to be consumed for on-road transportation, it can only achieve a blending of ~19.5%. Currently, Japan and China tap into used cooking oil (UCO) as their main feedstock for BD production, while India taps into other non-edible in- dustrial oils apart from UCO; at least 90% of the BD produced in Asia is still derived from edible oil sources with palm oil as the main resource tapped into by Indonesia, Malaysia, and Vietnam, while coconut is used

4**as the feedstock for BD** pro- duction **in the Philippines. This**

further drives the need to find alternative resources to support the production and use of BD in these countries. In Asia, a potential of at least ~6.2 hm3 could be produced based on the PR productions of 705 Tg in 2018 and at the lowest potential bran fraction of ~8 wt% and combined collection, processing, and conversion loss of ~20%. This quantity is about ~64% of the total BD production (~9.7 hm3) from prominent BD-producing countries in Asia. Generally, the potential amounts of BD that could be pro- duced from available RB in respective countries could signif- icantly contribute to their current biodiesel demand (Table 2). Among the BD-producing countries in Asia, only Japan has a declining potential to recover and produce BD from RB (Fig. 4g and Table 2). This is owing to the declining PR production Myanmar, Philippines, Vietnam 10 8 Myanmar Philippines Vietnam 6 4 2 0 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 Year c# 0.25 0.2 0.15 0.1 0.05 0 Year f* 0.5 0.4 0.3 0.2 0.1 0 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017

2018 Year Year h i containing a minimum of 15 wt% lipids). Error bars in a–c indicate the standard deviation of the data gathered from available sources; error bars in d–f indicate the reported production level, while columns indicate the local consumption of Japan, with an annual decrease in production rate by 0.4% (−0.14 Tg per year). Despite the declining potential, the avail- able potential RB that could be generated in Japan could enable the production (~0.058 hm3) of at least 3 times the current BD production (~0.017 hm3) in Japan. Likewise, the potential BD from RB in China and India in 2018 is ~1.5 and ~8.5 times more than their current consumption, respectively. For BD- consuming countries in Southeast Asia, Malaysia has the least potential BD (~0.024 to ~0.029 hm3) from RB. This is because Malaysia is among the countries producing the least amount of PR, while its consumption (0.66 hm3 in 2018) is among the highest. Among the Southeast Asian countries, Indonesia, the Philippines, and Thailand could on average contribute 20 to 80% of their on-road biodiesel consumption in 2018. Bangladesh and Myanmar currently do not produce or consume BD; the potential BD from RB in these countries could contrib- ute up to 30% (0.49 hm3) and 45% (0.23 hm3) of their on-road PD consumption of 1.66 hm3 and 0.46 hm3 in 2017 [27], re- spectively. Although there is no available information on the on-road PD consumption in Vietnam, 0.39 to 0.56 hm3 of BD could be potentially produced from locally generated RB from 2020 to 2040 if PR production continues to increase at the current rate. Overall, RB is a potential biodiesel resource, which Table 2 Biodiesel production and on-road consumption in Asia [28] and potential biodiesel from rice bran Regions in Asia/ Biodiesel 2008/2018 Countries Year Production Import Export Consumption On-Road Consumption hm3 hm3 hm3 hm3 hm3 % Blend (On-Road) Actual Mandate Potential BD from RB Lipids (hm3)a 2018 Linear Increase in Paddy Rice Production b 2020 2030 2040 Eastern China 2008 0.534 2018 0.834 0.000 0.853 0.000 0.357 0.534 1.330 0.160 0.313 0.20 0.20 n.a.c n.a. 2.045 1.877 2.334 2.150 2.539 2.370 2.745 2.591 Japan 2008 0.008 2018 0.017 0.000 0.001 0.000 0.006 0.008 0.011 0.008 0.009 0.00 0.03 n.a. n.a. 0.086 0.084 0.071 0.058 Southern Bangladesh 2008 - 2018 - - - - - - - - - - - - - 2.224 0.499 2.287 0.482 2.588 0.551 2.889 0.619 India 2009 0.075 2018 0.185 0.000 0.025 0.000 0.023 0.030 0.180 0.030 0.083 0.09 0.14 5.00 (2030) 1.527 1.594 1.799 2.003 Southeastern Indonesia 2008 0.630 2018 5.600 0.00 0.028 0.610 1.772 0.023 3.950 0.018 3.650 0.10 12.7 n.a. 20.0 1.954 0.735 2.063 0.723 2.370 0.833 2.677 0.943 Malaysia 2008 0.186 2018 1.245 0.000 0.000 0.198 0.585 0.000 0.660 0.000 0.660 0.00 7.00 5.00 10.0 0.024 0.025 0.027 0.029 Myanmar 2008 - 2018 - - - - - - - - - - - - - 0.225 0.280 0.321 0.362 Philippines 2008 0.066 2018 0.220 0.000 0.000 0.000 0.000 0.064 0.205 0.064 0.205 1.30 2.50 1.00 5.00 0.169 0.174 0.200 0.225 Thailand 2008 0.045 2018 1.567 0.000 0.002 0.000 0.001 0.447 1.568 0.265 0.920 2.50 6.50 2.00 6.5 - 7.0 0.285 0.327 0.368 0.410 Vietnam 2008 - 2018 - - - - - - - - - - - - - 0.390 0.422 0.491 0.559 a Expressed in hm3 (cubic hectometer or million cubic meter, MCM) as estimated from paddy rice production [26]; b linear regression (y) in million tons for a given year (x) (Eastern Asia: y = 2.2052x − 4203.9; R2 = 0.8208, China: y = 2.3663x − 4549.1; R2 = 0.8558, Japan: y = −0.1404x + 292.6; R2 = 0.8248, Southern Asia: y = 3.2329x − 6284.9; R2 = 0.9728, Bangladesh: y = 0.7372x − 1437.4; R2 = 0.9122, India: y = 2.2003x − 4273.5; R2 = 0.9609, Southeastern Asia: y = 3.2975x − 6439.5; R2 = 0.9738, Indonesia: y = 1.1783x − 2302.5; R2 = 0.9759, Malaysia: y = 0.0228x − 43.4; R2 = 0.7598, Myanmar: y = 0.4394x − 857.5; R2 = 0.8778, Philippines: y = 0.2777x − 542.3; R2 = 0.9534, Thailand: y = 0.4453x − 864.4; R2 = 0.8909, Vietnam: y = 0.7362x − 1441.8; R2 = 0.9349), assuming paddy rice with 14 wt% moisture [2], 8 wt% bran [2], with milling and logistic losses at 5%, and bran containing a minimum of 15 wt% lipids, at a lipid recovery of 95%, FAME yield of 0.88 w·w−1 , FAME density 880 kg/m3 , and availability and use factors of 1; c n.a. not available could be exploited by countries in PR-producing countries in Asia, specifically those in the South, East, and Southeast Asia. 3.3 Extraction and recovery of rice bran lipids The extraction of lipids is generally carried out by either me- chanical extraction or solvent extraction. Mechanical extrac- tion can be further categorized as static and dynamic pressing, which are carried out

13**with the use of** hydraulic press (**ram press) or screw press**

(extruder or expeller). From a preliminary study on RBL extraction with the aid of a hydraulic press that was reported in 1993, it was observed that 45% of the total available lipids could be extracted from RB with the resulting cake having ~16 wt% residual lipid content [59]. This result indicates the low recovery was not only achieved by hydraulic presses but also achieved with RB samples initially containing lipids of ~30 wt%. A more detailed investigation, which looked into different stabilization techniques and their influence on the later hydraulic extraction process, was reported by El-Kholy et al. [60] in 2009, where the extraction efficiency achieved, still, only reached ~47%. The same group of researchers also carried out extraction with a screw press which resulted in a maximum recovery of 40 wt% [61]. Unfortunately, both works reported by the same group of researchers did not indicate the initial lipid content of the RB used, which hindered objective comparison with reports from other works and between processes. However, it is of consensus from different studies that heat treatment before or during the mechanical extraction process improved oil yield from bran as the treatment softens the cells containing the lipids, freeing the lipids and easing their release during extraction [61–63]. For instance, cold pressing and untreated RB yielded 4 to 5.8 g lipid per 100 g RB, while hot pressing or RB with heat pre-treatment achieved yields up to 8.3 g lipid per 100 g RB [62–64]. Depending on screw press configuration and operating conditions, recoveries could vary from 37.5% [64] to as high as 53.7% [65] for RB containing lipids of ~22 to 24 wt%. Under favorable conditions, screw presses achieve relatively higher recoveries than hydraulic press and allow operations to be done continuously favoring large-scale operations and processes [66]. Mechanical extraction is favored in food and feed industries as it avoids the use of solvents and is often seen as a more environmentally friendly process. However, lipid recoveries of ~50% may not be favorable when producing high-volume and low-value products like biodiesel. Solvent extraction with the use of hexane, benzene, and others, with the former two seldom used nowadays owing to toxicity, is often adopted in the lab with the aid of a Soxhlet extractor to determine the total lipid content of lipid-containing samples like oilseeds. Although used as a reference method, the use of Soxhlet extractor is often limited in laboratories owing to the large volume of solvent required, long extraction times, and high energy requirements. Generally, solvent extraction enables higher lipid recovery compared to mechanical extraction and is often preferred for materials containing lipids less than 20 wt% [67]. Solvent extraction of RBL can be further categorized as conventional solvent extraction (CSE), sub-/super- critical solvent extraction (SSE), liquefied gas extraction (LGE), and aqueous extraction (AE). The different solvent extraction techniques may be carried out in a certain combination with various pretreatments including heat treatments, steaming, and hydrolysis. Extraction of lipids from RB with solvents is further enhanced in terms of extraction rate with the aid of irradiation including microwave and ultrasound irradiation to hasten the extraction process. A detailed review of green extraction technologies for RBL using solvents has been done by Garofalo et al. [68] in 2020. The brief review that will be presented hereafter will focus on the general idea of lipid extraction by solvents and key points not previously emphasized. Conventional solvent extraction of RBL is often carried out with solvents like hexane [69–71], ethanol [72, 73], and isopropanol [71, 74]. The use of alcohol in place of hexane is driven by concerns related to environmental emissions, related health risks, and flammability hazards in the use of n- hexane [71, 73, 74]. Comparison of extraction efficiency between isopropanol and hexane at ambient conditions was carried out by Proctor and Bowen [71], where these

1**solvents were found to be comparable**, achieving **extraction**

efficiencies over 90%. A separate work by Hu et al. [74] presented that the use of hexane have significantly higher efficiency (~85%)

1**than isopropanol** (~80%) **with extractions carried out at** 60 °**C. These discrepancies may have resulted**

because of differences in initial lipid contents and solvent-to-solid ratios (SSRs)

1employed, with the former employing an SSR of 10 cm3·g−1

with RB having 16.5 wt% lipids [71], while the latter employed SSR of 4.6 cm3·g−1 with RB having 24.9 wt% lipids [74]. With the use of aqueous ethanol containing ~6 wt% water, Oliveira et al. [73] reported that an extraction efficiency of 99.9% could be achieved

10at an SSR of 4 g·g−1 at 82 °C

for RB containing ~20 wt% lipids. Although the use of alcohol and aqueous systems has comparable apparent extraction efficiencies with n-hexane, the use of polar solvents risks the co-extraction of non-lipid components [75]. A more recent study by Capellini et al. [76] revealed that using ethanol and butanol could achieve extraction efficiencies of ~90%, but the extracts contained soluble proteins, with the oil fraction corresponding only to an extraction efficiency of ~80% for RB having a lipid content of 20.4 wt%. In CSE, extractions are often carried out at atmospheric pressure and temperatures

1from ambient to the near-boiling point of the chosen solvent

[69, 70, 72], and the presence of water in large quantities results in lower lipid extraction efficiencies [72, 73, 76]. Apart from the use of conventional liquid solvents for extraction, several studies have also considered the use of gases under sub-/supercritical conditions or liquefied state as extraction solvent. Among the gases explored as solvents are carbon dioxide, propane, butane, and petroleum gas. The idea of using supercritical carbon dioxide (SC-CO2) for RBL has been around since the 1980s, with SC-CO2 reported to achieve extraction yields of 22 g lipids per 100 gram RB and is comparable to hexane which yields 23 g lipids per 100 gram RB [77]. Although supercritical conditions of CO2 (31.06 °C, 7.37 MPa) are relatively low and easy to achieve, effective extraction of RBL lipids required SC-CO2 extraction operated at 60–80 °C and 30–50 MPa [68]. The high-pressure operation requirement is perceived to induce higher capital, operational, and maintenance cost [78]. Sparks et al. [78] have shown that similar yields (~22 g per 100 g RB) can be obtained with SC-CO2 and liquefied propane, but with propane extraction operated at 0.76 MPa as compared to 35 MPa required by SC-CO2. At 40 to 45 °C and 0.5 MPa, extraction with liquefied propane and butane can achieve similar extraction efficiencies of ~90%, with propane favoring the extraction of waxes, and butane favoring triglycerides [79]. Considering that liquefied petroleum gas (LPG) is primarily (~70%) comprised of propane and butane, Soares [80] proposed its use and achieved an extraction efficiency of ~82% at 30 °C and 1.5 MPa, which is comparable to SC-CO2 requiring 40 °C and 25 MPa. Safety precautions may have to be considered in the use of LPG and its constituents as these post certain risks or hazards in terms of fire and explosion. The main advantage in the use of these gases is on the ease of separation between the solvent and the crude extract upon decompression, without leaving toxic residue in the products. Water is often referred to as the “universal solvent” and has also been explored

1in the extraction of lipids from RB

. Unfortunately, the use of water in AE [81, 82], enzyme-assisted AE [83, 84], and subcritical water extraction [85], terminologies that are widely used in the literature related to lipid extraction, does not necessarily mean that water acts as the solvent. Aqueous extraction is often carried out at a high pH of 12 [81, 82] and its extracts are often characterized to have low FFA [81]. Often, these studies on lipid extraction do not provide analysis of the lipid composition and fatty acid profile, which gave no assurance that the extracts obtained are solely lipids. Moreover, with the extractions carried out at high pH, a fraction of the lipids may have been saponified which facilitated solubilization of the lipids in the aqueous phase. In most cases when enzymes like protease, cellulase, and amylase are added, the solid matrix which initially houses the lipids is generally broken down thereby releasing the lipids, but the lipids are not actually dissolved in water [84]. These approaches are reported to achieve an extraction effi- ciency of up to ~80%. Higher efficiencies of over 90% could be attained by enzyme-assisted AE [83] and subcritical water extraction [85] with the addition of hexane in the resulting mixture after RB have undergone the said treatments. Although both approaches are referred to as extraction, it in- volves the hydrolysis of the solid matrix which may have facilitated the release of the contained lipids, rather than the solubilization of the available lipids. Thus, studies on aqueous extraction of lipids may have to be revisited and reassessed if lipids are indeed being extracted by water or simply freed from the solid matrix that initially contains it. In view of scale-up and actual application, it is impor- tant to take into consideration two aspects of the extrac- tion process, namely, extraction kinetics, and equilibrium relationship. Studies involving lipid extraction kinetics of RBL, mechanisms, and equilibrium distribution of lipids between the miscella and the inert solid have been lim- ited. Majumdar et al. [72] in 1996 first reported the modeling of solvent extraction of rice bran lipids from pelleted-RB in a packed-bed system with hexane as the solvent, where the system was described with a one- dimensional model that accounted for the dynamic con- ditions of the system in terms of dimensionless transport quantities. In 2004, Amarasinghe and Gangodavilage [69]

1**looked into RB (pelleted)-hexane system, at a fixed temperature (60 °C) and using a Soxhlet extractor, where the process was found to follow a single-step first-order extraction rate**. However, **modeling a Soxhlet extractor as a strict batch process** may **not** be **appropriate** because **the extraction process involved** is **a**

1**semi-batch process** with **the products intermittently separated after each extraction cycle**

and is not limited by equilibrium. A pilot-scale extractor was also adopted for use with equilibrium ex- traction data provided in aid of equipment design [69].

1**More recent works published in 2017 involving RB- hexane** [70] **and RB (pelleted)-ethanol** [72] **systems have concluded that the extraction process involved more than** one **mechanism and is primarily governed by a rapid washing step and slower diffusion steps. However**

, there is a lack of consensus on this matter as there are still differences in the choices of models implemented by researchers. For example,

1**Zuniga-Diaz et al**. [70] **still opted to model the system according to a single diffusion model, while Kamimura et al**

. [72] and Bessa et al. [86] modeled the system adopting a 2-mechanism model. Bessa et al. [86] also carried out pilot-scale equilibrium experiments and determined that the pelleted-RB used required five ideal stages in a simulated counter-current extraction system with anhydrous ethanol as solvent. A pilot-scale extraction system involving SC-CO2 [87] and continuous microwave-assisted extraction of RBL with ethanol [38] were also reported, with efficiencies over 90%. Typical SSRs adopted during extraction ranged between 3 and 4 g solvent per gram RB. Although kinetic information and equilibrium relation are provided in cer- tain studies, it should be noted that this information and relationships are system-specific and would best be ob- tained through actual-scale experiments and/or with in- formation on mixing dynamics and flow characteristics. 3.4 Process options or synthesis routes for biodiesel production from rice bran lipids The conversion of RBL into BD could be achieved via various processes adopting different synthesis routes. To provide an objective basis when making comparisons be- tween processes, some reaction or process metrics com- monly adopted in biodiesel synthesis are briefly discussed. Any chemical reaction, including BD synthesis, requires the conversion of raw materials into products. A reaction

2**conversion is defined as the fraction of a** given **reactant**

(limiting reactant) at a given reaction period. Lipids are complex mixtures composed primarily of fatty acids (FAs) either in free or bound as esters. Also, some of these lipids produce more than one fatty acid alkyl ester (FAAE). These make it difficult to directly assess the conversion. Although several researchers have interchangeably used the conversion, yield, and FAAE content (CAE), these mea- sures are in principle different and are only interchangeable when pure reactants are used and under certain assump- tions. Considering that each FAAE is produced from a single fatty acid chain, monitoring the total fatty acids (TFA, free and bound) before the reaction (nTFAi) and after (nTFAf) the reaction would allow the determination of con- version (XTFA, Eq. 3). However, monitoring the unconvert- ed TFA after the reaction is not straight forward, and is often based on the amount of FAAE generated (nFAAE), with the assumption that available FAs are not degraded or transformed into forms that cannot be converted to FAAE. X TFA ¼ nTFAi −nTFA f nFAAE f −nFAAEi ¼ ð3Þ nTFAi nTFAi Depending on the synthesis routes and reaction schemes adopted, degradation or losses of reactant or product may occur. From a process perspective, it is often more practical to monitor and determine the amount of product that is pro- duced, which is often normalized and presented in terms of yields, which could either be relative to the theoretical maxi- mum product (YP, Eq. 4), initial lipid content (YL, Eq. 5), and dry solid or biomass processed (YS, Eq. 6). Each of these definitions for yield provides different prac- tical implications and serves as metrics for comparing differ- ent processes. As mentioned, each FAAE is generated from one FA chain, thus, making the moles of theoretical maximum FAAE (nFAAETheo), equal to the nTFAi. Given the abovementioned assumptions for estimating the conversion, this would then mean that YP and XTFA could be used inter- changeably in the context of BD production. Unlike XTFA, YP is a measure to indicate how far the desired reaction is from completion. Furthermore, YP could be determined based on the mass of FAAE (mFAAE) and TFA (mTFA) while incorporating a stoichiometric factor based on the average molecular weights of FAAE (MWTFA) and TFA (MWTFA), which could range from 1.04 to 1.07 for FAME and 108 to 114 for FAEE, with an average of around 1.05 and 109, respectively. Mass yields like YL, and YS are more practical measures to indicate the amount of FAAE that could be produced when processing a given mass of raw material, either the total amount of lipids (mLipid) or the dry solid or biomass (mBiomass _ Dry). Mass yields also allow comparisons with lipids undergoing refining after extraction and between the in situ process and conven- tional processes where lipids are first extracted with YL, and YS related to the amount of extractable or extracted lipids relative to the dry biomass processed. Furthermore, YL and YS may serve as indicators of variabilities in raw material quality. YP ¼ nFAAEf−nFAAEi ¼ nFAAEf−nFAAE i ¼ mFAAEf−mFAAEi ð4Þ nFAAETheo nTFAi mTFAi MWFAAE MWFA ¼ Y L ¼ Y S Y LTheo Y STheo Y L ¼ mFAAE f −mFAAEi ð5Þ mLipid Y S ¼ mFAAE f −mFAAE ð6Þ mBiomass Dry i ¼ Y L EL Although process responses are important indicators of how well the reaction and process has proceeded, it is also important to consider and account for the quality of the product, which is often expressed in terms of product purity or concentration of FAAE (CAE) in the hydrophobic product. Since authors of different researches have different prefer- ences in expressing their process responses, comparisons will be made in terms of the three different definitions for yields and purity. Responses not reported are calculated using the above definitions and based on available information provided in the different studies reported. Broadly, the different pro- cesses could be classified as conventional, in situ, and sub-/ supercritical processes. Apart from the typical processes of converting RBL to BD, emerging technologies or strategies will also be tackled in the review that follows. 3.4.1 Conventional (trans)esterif ication In this review, conventional (trans)esterification of RBL refers to the conversion of RBL to BD with the aid of either a homogeneous or heterogeneous catalyst carried out typically under ambient pressures and temperatures below the reaction mixture's boiling temperature. A sum- mary of published studies on the conventional synthesis or production of BD from RBL using homogeneous and heterogeneous catalysts are summarized in Tables 3 and 4, respectively. Conventional (trans)esterification of RBL catalyzed with homogeneous or heterogeneous catalysts typically employs the use of alcohols like methanol and ethanol as the alkyl donor. These catalyzed reactions may be further classified according to the type of catalyst employed, which could be broadly grouped into either base-, acid-, and enzyme-catalyzed (trans)esterifictaion. Homogeneous alkali or base-catalyzed Among the earliest investigation in the conversion of RBL to BD was the study by Bak et al. [88] in 1996, employing the use of base catalysts. The

13**most common homogeneous base catalysts** used **are** hy- droxides **and** methoxides **of** sodium and potassium **metals**

. Homogeneous base–catalyzed reactions require the use of re- fined RBO (RRBO) with FFA content less than 3 wt% found to achieve process and reaction yields of over 90% [89]. Base transesterification of RRBO is typically carried out at temper- atures (60 to 80°C)

25**near the boiling point of the**

alkyl donor for 45 min to an hour with

3**a molar ratio of** alcohol **to oil at** 6 to **9**

, a catalyst loading of 0.75 to 1 wt% of the available RRBO, and whenever possible, in the absence of water (Table 3). At the same catalyst loading, the yields achieved in decreasing order are observed using the following catalysts, $NaOCH_3 \geq NaOH > KOH$ [88]. The better catalytic performance observed with $NaOCH_3$ as a catalyst is because it readily dissociates into the active intermediate required for the transesterification reaction to proceed, while the use of hydroxides would require an additional step to form the methoxide intermediate. Between sodium and potassium hydroxide, higher amounts are gener- ally required for KOH to achieve similar yields with NaOH, as Table 3 Conventional and (trans)esterification of rice bran lipids using homogeneous catalyst* Feedstock Quality

2**Alkyl Donor and** a **Co-solvent** (cm3/g)**b** Solvent Loading **Catalyst**

Loading b Mixing / Irradiation / Heating

2**T (°C) / P (MPa) / t (h**

) c Space Loading / Reactor Loading d 0.08 0.28 M: F: - -

8**M: F: - - M: F**: - 1.4 **M: F**: - 0.66 **M: F: M: F**: - 0.05 **M: F**

: - - M: F: - 11.5 M: F: - 11.5 Methanol: Methanol: Methanol: Methanol: Methanol: Methanol: 0.24 - - 0.20 0.27 0.28 SLRn: 5 SLR: 0.24 SLRn: 9 SLR: ~0.41 SLRn: SLR: 6 - SLRn: 4.5 SLR: 0.20 SLRn: 6 SLR: 0.27 SLRn: 6 SLR: 0.28 Methanol OR 0.27 SLRn: 5.8 / 4 Ethanol 0.27 SLR: 0.27 Methanol: Methanol: Methanol: Methanol: 0.32 0.27 SLRn: 6 SLR: 0.32 SLRn: 6 SLR: 0.27 0.27* SLRn: 6 SLR: 0.27* 0.27* SLRn: 6 SLR: 0.27* NaOH/NaOCH3 1 wt.% of RBL NaOH 0.75 wt.% of RBL NaOH 0.75 wt.% of RBL NaOH 1.5 wt.% of RBL NaOH 0.5 wt.% of RBL NaOH 0.9 wt.% of RBL KOH 1.2 wt.% of RBL KOH 1 wt.% of RBL KOH 0.85 wt.% RBL NaOH 0.25 wt.% of RBL KOH 0.75 wt.% of RBL Mechanical Stirrer Mixing speed not specified Heating Mantle Mechanical Stirrer 1100 RPM Heating Mantle Magnetic Stirrer Mixing speed not specified Hotplate Magnetic Stirrer Mixing speed not specified Heating not specified Magnetic Stirrer 600 RPM Heating not specified Mechanical Stirrer 600 RPM Thermostatic Water Bath Mechanical Stirrer 600 RPM Hotplate Mechanical Stirrer 700 RPM Recirculating Bath Magnetic Stirrer 600 RPM Hotplate Water Bath Stirring not specified Hotplate Stirring not specified Hotplate T: 60 P: Ambient t: 1 T: 55 P: Ambient t: 1 T: 55 P: Ambient t: 1 T: 50 P: Ambient t: 1.5 T: 60 P: Ambient t: 1 T: 60 P: Ambient t: 2 T: 65 / 78 P: Ambient t: T: 60 P: Ambient t: 1 T: 40 P: Ambient t: 1 T: 45 P: Ambient t: 1 T: 45 P: Ambient t: 1 SL: n.a. f RL: -g SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: -g SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: - - 90 / 94 - - 90.18 - - 90 - 95 - ~98 - - - - ~80 - - - - - - - 91 / 92 - - - ≥98 - - - ~99 - - 65.3 - - 73.4 - [88] [89] [91] [92] [93] [193] [90] [34] [50] [47] Biomass Conv. Bioref. Feedstock Quality Alkyl Donor and Solvent Loading Catalyst Loading Mixing / Irradiation / Heating T (°C) / P (MPa) / t (h) c Space Loading / Reactor a Co-solvent (cm3/g)b b Loading d - 11.5 - - - -

8**M: F: - - M: F**: - 59 **M: F**: - 58 **M: F**: - 7/76 **M: F**

: - 32.9

8**M: F**: - 20 **M: F**: - 19 **M: F**

: - 20 Methanol: Methanol: Ethanol 0.41* SLRn: 9 SLR: 0.41* 0.28* SLRn: 6 SLR: 0.28* 0.32* SLRn: 5 SLR: 0.32* Methanol OR 0.23* SLRn: 5 / 9 Ethanol 0.58 SLR: 0.23 / 0.58 Methanol: Methanol: Step 1 Methanol: Step 2 Methanol: Methanol: 2 Steps Methanol: 3 Steps Methanol: 3 Steps Methanol: 3 Steps - - SLRn: 40 SLR: - SLRn: 15 SLR: - NaOCH3 0.75 wt.% of RBL KOH 0.5 wt.% of RBL NaOH 0.6 wt.% of RBL Stirring not specified Hotplate Ultrasonic Water Bath Flow Reactor Microwave Irradiated NaOH Magnetic Stirrer (Batch) 0.15-0.18 wt.% of RBL Microwave Irradiated H2SO4 5 wt.% RBL Magnetic Stirrer 600 RPM Hotplate Water Bath H2SO4 3 wt.% of RBL Not specified 0.38 SLRn: 5 / 9 H2SO4 0.42 SLR: ~0.80* 2 wt.% RBL Magnetic Stirrer 300 RPM Hotplate Oil Bath - SLRn: SLR: 6 / 7.5 - H2SO4 0.5 wt.% of RBL NaOCH3 Mechanical Stirrer 600 RPM Heating Mantle 0.88 wt.% of RBL - - SLRn: - SLR: 0.08 / SLRn: 0.07 / 0.22 7 / 6 / 6 H2SO4 0.5 wt.% of RBL NaOH 1.1 wt.% of RBL H2SO4 Mechanical Stirrer 600 RPM Thermostatic Water Bath Mechanical Stirrer SLR: - Loading not specified 400 RPM - SLRn: SLR: NaOH Thermostatic Water Bath 1.1 wt.% of RBL 6/7/6 H2SO4 Mechanical Stirrer - 1 wt.% of RBL 600 RPM KOH Thermostatic Water Bath 0.75 wt.% of RBL T: 46 P: Ambient t: 1 T: 55 P: Ambient t: 0.8 T: 50 – 73 P: t: 0.02 – 0.11 - T: 60 – 80 P: t: 0.08 – 0.33 - T: 60 P: Ambient t: 5 T: 55 - 60 P: Ambient t: 4 T: 60 / 100 P: Ambient / - t: 2 + 6 / 8 T: 65 / 55 P: Ambient t: 1 + 1 T: 55 - 60 P: Ambient t: 1 + 1 + 1 T: - / - / 55 P: Ambient t: 1.25 + 1.25 + 1 T: 50 / 50 / 60 P: Ambient t: 1 + 1 + 0.75 SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - SL: n.a. f RL: - YS: YL: YP: CAE:

YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: - 96.5 - - 94 - - - - -≥99 - - 95 – 98 - - - - ~99 - - 72 - - - - - CAE: 96 YS: - YL: 83.3 YP: - CAE: - YS: - YL: 90 YP: - CAE: - YS: - YL: 87 YP: CAE: - YS: 98.7 YL: 98.3 YP: CAE: [157] [94] [95] [30] [96] [97] [98] [46] Biomass Conv. Bioref. Feedstock Quality Alkyl Donor and Solvent Loading Catalyst Loading Mixing / Irradiation / Heating T (°C) / P (MPa) / t (h) c Space Loading / Reactor a Co-solvent (cm3/g)b b Loading d - Methanol: 0.41* SLRn: 9 115 SLR: 0.41* Lipase (A. niger) 1.25 wt.% of RBL Incubator Shaker Stirring not specified T: P: t: 30 Ambient 96 SL: RL: - - Methanol: 0.19* SLRn: 4 SLR: 0.19* DBTDL (MW: 631.56) Magnetic Stirrer 1 mol : 400 mol RBL Stirring not specified Heating not specified T: 60 P: Ambient t: 4 SL: RL: n.a. f - n.a. f - YS: - YL: 41.7 YP: CAE: - YS: - YL: 68.9 YP: CAE: - * Entries to the table are calculated based on available information to facilitate comparison; a Rice bran lipids quality in terms of moisture content (M, wt.%), free fatty acid content (F, wt.%); b Alkyl donor and co-solvent relative to the mass of lipid or oil used (cm3 /g), solvent loading as expressed in terms of solvent-to-lipid molar ratio (SLRn), solvent-to-lipid volume to mass ratio (SLR, cm3 /g); c Temperature (T), pressure (P), and time (t); d

2**Space loading** (expressed **as the reactor volume to the amount of biomass loaded**, cm3 /g), and **reactor**

loading (percentage of the reactor volume occupied by the reaction mixture); e Yields expressed as the amount of FAAE relative to the solid (YS), relative to the total lipids (YL), and relative to the theoretical maximum amount of alkyl ester (YP), with purity (CAE) expressed as the alkyl ester content; f not specified (n.s.) and not applicable (n.a.); g incomplete information to allow estimation with much longer reaction periods of 8 to 24 h or even longer, 2 to 5 wt% and

16**molar ratio of methanol to oil** of 10 **to** 40, **at** a reaction **temperature of** ~60 °**C**

, higher catalyst loading of in 2005. Compared to homogeneous base–catalyzed reactions H2SO4 as catalyst was first explored by Zullaikah et al. [30] and degummed RBO (DDRBO) to FAME with the aid of by several researchers. The (trans)esterification of dewaxed use of mineral acids, specifically H2SO4, has been explored catalyst and bring the reaction to a halt. To address this, the and hydrolysis that would eventually consume the available which results in a chain of reactions involving saponification base catalysts is the reactivity of the catalyst towards FFA, Homogeneous acid-catalyzed The main challenge in using NaOH and KOH as the catalyst, respectively [89]. of ester produced to a minimum of 5% and 10% when using carried out with gentle mixing to keep the losses in the amount present in the system. It is recommended that washing be saponification (fatty acid, NaOH/KOH, and water) are all formation of soap considering that the reactants required for ferred that the emulsion observed may have also involved the Although not further analyzed and confirmed, it could be in- in FAAE, with observed formation of emulsion [89]. mixing during the washing step is found to incur large losses the unreacted alcohol, and the loaded catalyst. Rigorous water to facilitate the separation of the by-product (glycerol), transesterification reaction is generally washed with warm the crude product. The reaction mixture resulting from the and/or FFA but could also occur in the recovery of FAAE in served during the transesterification in the presence of water availability and lower cost. Saponification is not only ob- ly used in the transesterification of refined oils owing to its However, compared to methoxides, hydroxides are still wide- the presence of significant quantities of FFA (11.5%). (65 to 73%) when compared to sodium methoxide (96.5%) in [47], it was found that hydroxides generally have lower yields the AG molecules. In an optimization study by Mumtaz et al. and subsequent saponification of the available fatty acids from a by-product of alkoxide formation, would induce hydrolysis loading of over 1 wt% resulted in yields below 90%. Water, as et al. [93], and Sinha et al. [89], it was observed that NaOH works by Krishnakumar et al. [91], Eevera et al. [92], Ahmad would promote the saponification process to occur. In separate ides and alcohol results in the formation of water, which that the formation of alkoxide moieties upon mixing hydrox- comparable performance with NaOCH3, it should be noted Although the use of sodium hydroxide is found to have same molar loading. same weight loading and should instead be compared at the difficult to directly compare the performance of catalysts at the and higher molecular weight than NaOH. This also makes it [90]. This is because KOH is available at lower purity (~85%) observed from the works of Mumtaz et al. [47] and Prabu et al. Biomass Conv. Bioref. Table 4 Conventional and (trans)esterification of rice bran lipids using heterogeneous catalyst* Feedstock Quality a Co-solvent (cm3/g) b Alkyl Donor and Solvent Loading Catalyst Loading b Mixing / Irradiation / Heating T (°C) / P (MPa) / t Space Loading / Reactor (h) c Loading d 1–99 - Methanol Steps - Methanol - - SLRn: SLR: 1.6/ 3.6 Novozym 435 - 5 wt.% of RBL 0.23* SLRn: 5 SLR: 0.23* Novozym 435 4 wt.% of RBL Magnetic Stirrer 150 RPM Hotplate Water Bath Incubator Shaker 200 RPM - Ethanol 0.47* SLRn: 7 - SLR: 0.47* Lipozyme TL-IM 4 wt.% of RBL Incubator Shaker 200 RPM M: - n-Butanol 0.94* SLRn: 9 F: - SLR: 0.94* Lipozyme RM-IM 4 wt.% of RBL Incubator Shaker 200 RPM M: F: 10 – 40 Methanol n.s. Hexane 0.1 SLRn: 2 Candida sp. 99-125 2 SLR: 20 wt.% of RBL Incubator Shaker 170 RPM M: F: - Methanol 0.27* SLRn: 6 11.5 SLR: 0.27* Novozym 435 Incubator Shaker 1 wt.% of RBL Stirring not Specified M: F: 4 54 Ethanol 0.83* SLRn: 4 SLR: 0.83* Lypozyme TL IM 0.5 g Packed-Bed Reactor L = 5.1 cm; D = 0.48 cm Recirculating Water Bath M: F: - - Ethanol 0.60* SLRn: 9 SLR: 0.60* CaO 3 wt.% of RBL Mechanical Stirrer 600 RPM Hotplate Water Bath M: F: - - Methanol 1.62* SLRn: 35 SLR: 1.62* Calcined Seashell 0.5 wt. % Magnetic Stirrer 150 RPM Heating Mantle M: F: - 0.05 Methanol: 0.69* SLRn: 15 SLR: 0.69* Calcined Coral 100 wt.% of RBL Stirring not Specified Heating not Specified M: F: - - Methanol: M: F: - - Methanol: 0.69* SLRn: 15 SLR: 0.69* 0.42* SLRn: 9 SLR: 0.42* Calcined Egg Shells w/ Silver Nanoparticle 2 wt.% of RBL K-ZnO 5 wt.% of RBL Magnetic Stirrer 600 RPM Hotplate Magnetic Stirrer Stirring not Specified T: 50 P: t: 4 – 6 Ambient T: 30 - 35 P: Ambient t: 6 T: 30 - 35 P: Ambient t: 6 T: 30 - 35 P: Ambient t: 6 T: 40 P: Ambient t: 10 T: 30 P: Ambient t: 96 T: 20 P: - t: 4 T: 70 P: Ambient t: 2 T: 65 P: Ambient t: 2 T: 65 P: Ambient t: 2 – 4 T: 65 P: Ambient t: 6 T: 65 P: Ambient SL: RL: SL: RL: SL: RL: SL: RL: SL: RL: SL: RL: SL: RL: SL: RL: SL: RL: SL: RL: SL: RL: SL: RL: n.a. f - g

5**n.a**. f **n.a**. f **n.a**. f **n.a**. f **n.a**

. f

5**n.a**. f **n.a**. f **n.a**. f **n.a**. f **n.a**

. f n.a. f YS: - YL: YP: ≥95 - CAE: ≥95 YS: - YL: - YP: 45 – 55 CAE: - YS: - YL: - YP: 45 – 55 CAE: - YS: - YL: - YP: 45 – 55 CAE: - YS: - YL: 87.4 YP: - CAE: - YS: - YL: 89.3 YP: - CAE: YS: - YL: - YP: - CAE: 92 YS: - YL: - YP: 70 CAE: - YS: - YL: - YP: - CAE: 95 YS: - YL: - YP: >98 CAE: - YS: - YL: ~92 YP: - CAE: - YS: - YL: - [33] [47] [103] [155] [104] [105] [106] [107] Biomass Conv. Bioref. Feedstock Quality a Alkyl Donor and Solvent Loading Catalyst Loading Mixing / Irradiation / Heating T (°C) / P (MPa) / t Space Loading / Reactor Co-solvent (cm3/g) b b (h) c Loading d M: - Methanol: 0.69* SLRn: 15 F: 0.28 SLR: 0.69* KI/Al2O3 5 wt.% of RBL Hotplate Oil Bath Stirring not Specified Heating not Specified M: F: - Methanol: 0.23* SLRn: 5 - SLR: 0.23* ZrO2-Ash n.s. Stirring not Specified Heating not Specified

8**M: F: - - M: F: - - M: F: - - M: F**: - - M: F: - - **M: F**

: - - Methanol: Methanol: Methanol: Methanol: Methanol: 0.69* SLRn: 15 SLR: 0.69* 0.56* SLRn: 12 SLR: 0.56* 0.46* SLRn: 10 SLR: 0.46* 0.42* SLRn: 9 SLR: 0.42* 0.27* SLRn: 6 SLR: 0.27* Methanol: - SLRn: 14 Esterification only SLR: - SBA-15 0.1 wt.% of RBL NaOH 1 wt. % of RBL KNO3-Zeolite 10 wt. % of RBL Stirring not Specified Heating not Specified Magnetic Stirrer Stirring not Specified Hotplate Water Bath K2CO3-Zeolite 4 wt. % Magnetic Stirrer 500 RPM Hotplate Carbonized Palm Shell Magnetic Stirrer Modified with CaO Stirring not Specified Activated with KOH Hotplate Oil Bath 8 wt.% of RBL Ni-Schiff Base Chelate

300 RPM 0.5 wt.% of RBL Ni acetate 1 wt % of RBL Cs1H2PW12O40 0.041 g· cm-3 Parr Reactor 100- cm3 600 RPM M: F: - 11 M: F: - 14 M: F: - 14 Methanol: 2 steps Ethanol: 2 steps Ethanol: 2 steps - SLRn: SLR: 0.68 0.68 10 / 40 - SLRn: 3.6:1 SLR: 0.68 SLRn: 3.6:1 SLR: 0.68 Step 1: H3PW12O40/SiO2 Parr 4590 Reactor 3 wt.% of the RBL 300 RPM Step 2: Mg0.71(Al)0.24La0.05 3 wt.% of the RBL Step 1: PK208LH Batch Reactor 77 wt.% RBL* 150 RPM Step 2: PA306S Thermal Bath 77 wt.% RBL* Step 1: PK208LH 55.5 grams 10 cm3·min-1 Packed-Bed Reactor Step 2: PA306S Recirculating water bath 33 grams t: 3 T: Reflux P: Ambient t: 8 T: Reflux P: Ambient t: 3 T: 70 P: Ambient t: 1 T: 67.5 P: Ambient t: 4 T: 65 P: Ambient t: 3 T: 65 P: Ambient t: 6 T: 65 P: Ambient t: 2 T: 65 P: Ambient t: 4.2 T: 70 / 100 P: Ambient / - t: 4 + 9 T: 50 / 50 P: Ambient t: 12 + 2 T: 50 / 50 P: - t: 5.1 + 3 SL: RL: n.a. f SL: RL: n.a. f SL: RL: n.a. f SL: RL: n.a. f SL: RL: n.a. f SL: RL: n.a. f SL: RL: n.a. f SL: n.a. f RL: -g SL: RL: n.a. f SL: RL: n.a. f SL: RL: n.a. f YP: 95.5 CAE: YS: - YL: 95.2 YP: - CAE: - YS: - YL: ~96* YP: - CAE: 100 YS: - YL: 91 YP: 98.6 CAE: YS: - YL: 83.2 YP: - CAE: - YS: - YL: 98.18 YP: - CAE: YS: - YL: - YP: 95 CAE: - YS: - YL: 93.5 YP: - CAE: - YS: - YL: - YP: 92.4 CAE: - YS: - YL: 78 YP: - CAE: 97 YS: - YL: - YP: ~98 CAE: High YS: - YL: - YP: ~98 CAE: High [108] [109] [111] [112] [35] [113] [114] [123] [36] [110] Biomass Conv. Bioref. Feedstock Quality

2**a Alkyl Donor and Co-solvent** (cm3/g) **b** Solvent Loading **Catalyst**

Loading Mixing / Irradiation / Heating T (°C) / P (MPa) / t Space Loading / Reactor Yields and Purity Ref. b (h) c Loading d e - Methanol: 0.46* SLRn: 10 Carbonized Rice Chaff ns SLR: 0.46* Sulfonated with H2SO4 1.5 wt.% of RBL Magnetic Stirrer Stirring not Specified Hotplate T: 65 P: Ambient t: 6 SL: RL: M: 0-3 Methanol: 1* SLRn: 12 F: 30-40 SLR: 1* HClSO3-ZrO2 6 wt.% of RBL Stirring not Specified Heating not Specified T: P: t: 120 - 12 SL: RL: - Step 1 SLRn: 8/6 22 Ethanol SLR: - Step 2 Methanol Fe2(SO4)3 450 RPM 3 wt.% of RBL Heating not Specified KOH 1.75 wt.% of RBL T: Reflux / 60 P: Ambient t: 3 + 1 SL: RL: n.a. f n.a. f n.a. f YS: - YL: - YP: 97.2 CAE: - YS: - YL: - YP: >92 CAE: - YS: - YL: - YP: - CAE: 96.6 * Entries to the table are calculated based on available information to facilitate comparison; a Rice bran lipids quality in terms of moisture content (M, wt.%), free fatty acid content (F, wt.%); b Alkyl donor and co-solvent relative to the mass of lipid or oil used (cm3 /g), solvent loading as expressed in terms of solvent-to-lipid molar ratio (SLRn), solvent-to-lipid volume to mass ratio (SLR, cm3 /g); c Temperature (T), pressure (P), and time (t); d

2**Space loading** (expressed **as the reactor volume to the amount of biomass loaded**, cm3 /g), and **reactor**

loading (percentage of the reactor volume occupied by the reaction mixture); e Yields expressed as the amount of FAAE relative to the solid (YS), relative to the total lipids (YL), and relative to the theoretical maximum amount of alkyl ester (YP), with purity (CAE) expressed as the alkyl ester content; f not specified (n.s.) and not applicable (n.a.); g incomplete information to allow estimation Biomass Conv. Bioref. H2SO4 via a single or 2-step esterification process, and use reduce the FFA content to less than 1% with 0.5 to 1 wt% reaction time of 8 to 10 h. An alternative approach is to allowing a high degree of conversion (> 95%) within a total the transesterification step resulted in reduced reaction time 96% FAME after 6 h. An increase in temperature during temperature of 100 °C to achieve a product containing methanol to AG ratio of 9 and allowed to react under a (AG) was then further subjected to transesterification at product containing 65% FAME and 35% acylglyceride content from 50 to <1% in 2 h at 60 °C. The resulting 2 wt% H2SO4 to convert 98% of the FFA, reducing the FFA the (trans)esterification at methanol to FFA ratio of 5 and overall reaction time, Zullaikah et al. [30] first carried out multiple-step approaches have been explored. To reduce the convert all available fatty acids in the RBL samples to BD, that conventional one-step approaches could not effectively Homogeneous multi-step acid- and base-catalyzed Given [30, 95]. period of 2 to 4 h even at high FFA contents of over 50% content in RBL samples which could be achieved in a short H2SO4 would best be adopted for reduction of the FFA librium yields. For conventional processes, the use of of H2SO4 than DBTDL, it can achieve much higher equi- the reaction being reversible [39]. Despite the lower activity yields to less than 20%, which authors have attributed to prolonged reaction time resulted in a drastic decrease in as it had good solubility in the reactants. Unfortunately, (~70%) than H2SO4 (~40%) during transesterification [39], alternative catalyst that was found to achieve better yields (DBTDL), which is a Lewis acid, has been explored as an an organo-tin compound, specifically dibutyltin dilaurate and higher methanol to lipid ratio of 40. Apart from H2SO4, verted to FAME within 5 h at higher acid loading of 5 wt% that RBL samples with 59% FFA could be completely con- later work by Ju and Zullaikah [94] in 2013, it was found requiring more alcohol to ensure complete conversion. In a total fatty acid ratio with samples having more triglycerides oil molar ratio as this would translate to different alcohol to straightforward and should not be done at fixed alcohol to FFA content, comparison of reaction performance is not much longer reaction times. With samples having different within 8 to 24 h, with samples having lower FFA requiring could achieve products with FAME contents over 90% molar ratio of 10, DDRBO samples with FFA over 63% work of Zullaikah et al. [30], at the same methanol to oil transesterification of FFA-containing RBL sample. In the FFA, allowing the simultaneous esterification and an acid catalyst is its ability to catalyze the esterification of than conventional bases used. The main advantage of using are not sensitive to FFA, its catalytic activity is much less are required (Table 3). Although acid catalysts like H2SO4 Biomass Conv. Bioref. alkali catalyst in the subsequent transesterification step to con- vert the remaining AGs, following typical alkali catalyzed transesterification [46, 96–98]. Generally, the total time re- quired for the reactions ranged from 2 to 3.5 h, which is much lesser than using a single catalyst. Although these approaches have been successfully carried out in the lab, these may have to be reassessed for large-scale adaption considering the addi- tional separation processes required between steps due to em- ployment of 2 different types of catalysts, losses in the reac- tants between steps, and additional pieces of equipment required. A persistent concern

20**in the** use **of** homogeneous **alkali** and **acid catalyst** is **the** generation **of**

either basic, acidic, or salt- containing wastewater, especially in a paradigm where envi- ronmental impact and sustainability are of utmost concern. An environmentally benign and renewable catalyst for (trans)esterification is

15**lipases (E.C. 3.1.1.3), a**

group of en- zymes part of carboxylesterases. The use of free lipase like the one obtained from Aspergillus niger is capable of achiev- ing a yield or conversion of ~42% at 30 °C, over a reaction time of 96 h [47]. The use of lipases allows the (trans)esterification to be carried out under milder conditions (30 to 50 °C), but its use is often hindered by its high cost, non-reusability, poor tolerance to alcohols, and low heat sta- bility [99, 100]. A workaround on the common concern for homogeneous catalyst concerning their renewability, separa- tion, recovery, reuse, and cost, is the immobilization of these catalysts or the use of their heterogeneous counterparts. Studies

21**concerning the use of heterogeneous catalysts in** the conversion **of**

RBL into BD are summarized in Table 4. Immobilized lipase-catalyzed Commercial immobilized (IM) lipase widely adopted in catalyzing (trans)esterification of lipids to BD include those produced by Novozymes (

15**Novozym® 435**, Lipozym® **RM-IM**, Lipozym® **TL-IM**

), Amano (Lipase PS Amano IM), and by

15**Beijing University of Chemical Technology** (textile membrane IM **Candida sp. 99-125**

lipase) [99]. Among the commercialized IM lipases, only Lipase PS Amano IM with lipase from Burkholderia cepacia has not been explored in the (trans)esterification of RBL to BD. Around the same time, H2SO4 was investigated for the (trans)esterification of RBL to BD, IM lipases Novozym® 435 (Candida antarctica lipase form B), and Lipozym® RM IM (Rhizomucor miehei lipase) as catalysts have been explored by Lai et al. [101]. It was found that pretreatment of the IM lipases by soaking in tert-butanol and the lipid substrate demonstrated better activities and higher equilibrium yields. At the same catalyst loading, of 5 wt% relative to the available RBL, higher FAME content (>95%) was achieved using Novozym® 435 as compared to Lipozym® RM-IM (~80%). Furthermore, it was also ob- served that the presence of wax esters and phospholipids re- sulted in certain inhibition of Novozym® 435, and intermittent dosing of methanol was found advantageous in maintaining the activity of the lipase. Novozyme-catalyzed esterification of RB FFA was also observed by Lai et al. [101] to proceed faster as compared to transesterification of RB triglycerides (TG), requiring 1 h and 6 h of reaction time, respectively, to achieve a FAME content of ~95% in the product. However, RBL samples with different proportions of FFA and AGs require a two-step process, to accomplish the ester- ification and transesterification as the water generated during esterification of the available FFA slowed down the transesterification process of the AGs. Nevertheless, even with a two-step process, up to ~98% FAME in the product could be achieved.

6**In a separate work by** Rodrigues **et al**. [102], **the**

3 com- mercial lipases were found to have a different preference in the type of alcohol used during transesterification of RBO, with Novozym® 435, Lipozym® TL-IM (Themomyces lanuginose lipase), and Lipozym® RM-IM having better affinities to methanol, ethanol, and n-butanol, respectively. Despite introducing excess amounts of alcohol, 2 to 3 times of the stoichio- metric requirement, and reaction time for up to 6 h, the yields achieved were only about 35 to 45%,

6**at a catalyst loading of** 4 **wt**

%. In the optimization study conducted by Muztaz et al. [47] using Novzym® 435,

6**at a catalyst loading of** 1 **wt% and methanol to** RB TG **molar ratio of**

6, it required 96 h to achieve a conversion or yield of ~89%. These results further imply possible inhibitory effects of excess alcohols as ob- served by Lai et al. [101]. This phenomenon was also ob- served by Li et al. [33] when working with a novel IM lipase from Candida sp. 99-125. Furthermore, intermittent dosing of alcohol employed by Lai et al. [101] only required methanol to lipid molar ratio of 1.6 and 3.6 for FFA and TG, respec- tively, while Li et al. [33] reported the use of methanol to lipid molar ratio of 2 in a lipid sample containing FFA and AGs. Thus, the amount of alkyl donor introduced in enzyme cata- lyzed (trans)esterification should be near the stoichiometric requirement and favorably introduced in several dosing to minimize possible inhibitory effects. Apart from the lesser amount of alcohol that would be required to achieve high yields, IM lipases also have the ad- vantage of being reused. Different lipase-catalyzed transesterification systems may differ in the extent of reusing the IM lipases. For instance, Lai et al. [101] reported that Novozym® 435 retained 90% of its catalytic activity after 14 cycles of use, while Lipozym® TL-IM was reused up to 27 cycles while maintaining 82% of its activity [103], and Li et al. [33] reporting the reusability of up to 7 times with their novel IM lipase from Candida sp. 99-125 maintaining 90% of its initial activity. Also, it was observed that IM lipases re- quired washing with certain organic solvents to maintain high activities during reuse as by-products like glycerol and water may coat the immobilization matrix or inhibit the lipases and, thus, reduce the overall activity. The most commonly used or Biomass Conv. Bioref. preferred solvents include tert-butanol and n-hexane for Novozym® 435 [101, 102], ethanol, and hexane for both Lipozym® TL-IM and RM-IM [102, 103]. The reusability of IM lipase is an important economic factor for the BD pro- duction process as IM lipases may cost from 2.5 USD to as high as 32 USD per kg of BD produced for single use and would require 20 to 320 of reuse without loss in catalytic activity to lower the cost of the enzyme to about 0.1 USD per kg of BD to make it economically competitive [99]. A direct comparison between the performances of different IM lipases is not straight forward. The activities are not only dependent on their affinity to the alcohol used, and substrate quality, but also influenced by various factors including water content in the reaction system [33, 103], temperature [102, 103], and other operational parameters, including but not lim- ited to reactor design, and activation and regeneration proto- cols [101–103], which often have synergistic effects on the overall performance of a given lipase. A means to ease out comparisons between lipases is to report the activity and the corresponding standard activity assay adopted and indicate enzyme loadings in terms of lipase activity rather than in mass percentages, apart from the reaction conditions and systems employed. A detailed and thorough review of IM lipase-catalyzed BD production using various substrate was written by Zhao et al. [99] and accounts not only for the technical aspect in IM lipase-catalyzed BD production but also the eco- nomic implications and its current state in terms of industrialization. Heterogeneous alkali/base-catalyzed Compared to IM li- pases, the exploration and use of heterogeneous alkali cata- lysts came much later around 2009. Generally, these catalyst may further be classified as alkaline (CaO [104–106]), transi- tion metal (ZnO [107]), or mixed-metal (Mg-Al-based [36, 108], ZnO-based [107], ZrO2-based [109]) oxides, hydrotal- cite [36], ion-exchange resins (PA306S [110], and SBA- 15[111]), zeolite-based [35, 112], impregnated or activated carbon [113], and Ni-Schiff base chelate promoter with Ni(CH3COO)2·4H2O [114]. Heterogeneous alkali-catalyzed transesterification typically requires 2 to 9 h, 0.5 to 100 wt% of catalyst, and alcohol

12**to oil molar ratio of 5**

to 35, achieving yields from 70 to 98% (Table 4). Compared to a homogeneous catalyst, heterogeneous counterparts have lower activities generally owing to mass transfer limitations, which would require either more catalyst, longer reaction time, or higher quantities of alcohol to overcome. For certain catalysts, even under favorable conditions to catalyze the transesterification of refined RBL, yields achieved may be lower. Among the many alkaline earth metal oxides, CaO as a heterogeneous catalyst has been the most widely explored primarily owing to its high activity [115]. To address the re- newability challenge of a homogeneous alkali catalyst, CaO could be derived from renewable sources including coral fragments [104], seashells (Chicreus brunneus [105]), and eggshells [106]. Calcium in these biological sources is gener- ally in the form of CaCO3 and would require pretreatment by heating to a temperature between 700 and 1100 °C to produce the desired CaO and remove other impurities [104, 106, 113]. Although the main active component is the same for the three derived catalysts and is capable of achieving yields or FAME content in the product of over 95%, their required catalyst loading, methanol to lipid ratio, and reaction time were very different. For instance, the use of coral-derived CaO required up to 100 wt% catalyst [104] as compared to those derived from seashell and eggshell which only required a catalyst loading of no more than 2 wt% [105, 106]. One main differ- ence is the calcination process adopted, where those requiring lower catalyst loading have derived their catalyst by calcina- tion of the raw material at temperatures of at least 800 °C [106], and as high as 1100 °C [105]. From the study by Rizkianto et al. [106], calcination at temperatures between 800 and 1000 °C did not influence the catalytic activity of the derived CaO, but a slower rate of heating (5 °C/min) dur- ing the calcination process and impregnation with silver nano- particles before calcination was favorable in improving the yield. In the work of Mazaheri et al. [105] with C. brunneus shells, it was found that calcination temperatures at 1100 °C resulted in BD with a kinetic viscosity that could meet stan- dard requirements. The actual performance of the heterogeneous catalyst may be influenced by various factors including chemical (functional groups, chemical composition), morphological (geometry and particle size), and textural (pore size, pore volumes, surface area, surface charges) properties of the catalyst, but many of these properties are either not reported or methods of determination are not in consensus. Nevertheless, these catalysts have been reported to be reusable, but would overtime require regeneration by subjecting the catalyst to the calcination process. This type of catalyst could retain its activity, with yields above 90% for about 3 to 5 cycles before eventually deactivating, which could be caused by either the formation for $Ca(OH)_2$ and subsequently reverting to $CaCO_3$ [104] or the leaching of calcium into the reaction medium and changes in the morphology of the catalyst [105]. Alkali and alkaline earth oxides or hydroxides exhibit certain solubility in alcohols or the reaction medium. Transition metal oxides like ZnO are reported to be insoluble when used in systems to produce BD and is considered to have low toxicity [107]. Other transition metals include Al_2O_3 [107] and ZrO_2 [109]. However, these transition metal oxides have lower basicity as compared to alkali or alkaline earth metal oxides but may serve as good porous support [107]. In most cases, transition metal precursors are first calcined at 450 to 550 °C to produce the desired metal oxide support, then impregnated with a more active metal catalyst, and finally calcined at 500 to 600 °C for 2 to 5 h to produce the desired mixed-metal oxide [36, 107, 108]. Although calcination temperature and time vary between the metal precursors used, appropriate temperature and time should be determined to avoid decomposition of the active agent and annealing of the particles, which would result in poor catalytic activities for mixed metal oxides [107]. Several combinations have been explored including Mg/Al oxide with Cs, Ba, Sr, and La [36], ZnO_2 impregnated with KOH [107], Al_2O_3 impregnated with KI [108], and ZrO_2/SiO_2 [109]. In their investigation, Chuayplod et al. [36] have found that impregnation improved the native activity of metal oxide, with Cs impregnated $Mg_{0.72}Al_{0.28}$ oxide being more active when compared to those impregnated with La, yielding 62 and 50% methyl butyrate, respectively, during the methanolysis of tributyrate as compared to the native $Mg_{0.72}Al_{0.28}$ oxide. To avoid the need of carrying out calcination of the metals, it is also possible to prepare mixed metal catalyst in hydrotalcite form via alkali-free co-precipitation to produce $Mg_{0.69}(Al)_{0.18}La_{0.13}$ which could achieve methyl butyrate yields of up to 98% in 3 h. Both Al_2O_3 impregnated with KI and ZnO impregnated with KOH were found to have marked increases in their basicity expressed as basic sites, which were 1.4 and 7.9 mmol g^{-1}, respectively [107, 108]. Compared to native ZnO which is found to have a basic site of 3.6 mmol g^{-1} [107], no basic sites were detected from Al_2O_3 [108]. Both reports indicate that the active agent apart from the native metal support is K_2O which was expected to form during calcination [107, 108]. Another mixed-metal oxide is ZrO_2/SiO_2, which was successfully synthesized by Fatimah et al. [109]. Interestingly, a comparable catalyst could be produced replacing commercial sources of SiO_2 with silica rich ash derived from bamboo leaves. Although the synthesis and subsequent use of mixed-metal oxides to convert RBL to BD were successfully carried out in the above studies, achieving yields or products with FAME contents of over 95%, their reusability were not reported. Apart from metals, ion-exchangers based on polymeric resins, silica, and zeolite have also been explored. Strong base anion (SBA) exchangers like DIANION™ PA306S (trimethyl ammonium functionalized Styrene-divinylbenzene copolymer) [110] and SBA-15 (Mesoporous SiO_2) [111] have been used in the transesterification of AGs in RBL with alcohol. In the work of Shibasaki-Kitakawa et al. [110], it was found that SBA resins were capable of adsorbing FFA in the reactant and the later by-product glycerol. This inherent characteristic of SBA may be taken advantage of not only to catalyze the reaction but also as a simultaneous purification process. However, the use of SBA like that of PA306 would require a high catalyst loading of over 70 wt%. For SBA-15, only 0.1 wt% was required but was used along with 1 wt% loading of NaOH [111]. Although Nrayama et al. [111] have shown that the addition of SBA-15 in the reaction mixture could improve the yield from ~80% with 1 wt% NaOH alone to a yield of 91% in the presence of SBA, there was no explicit information regarding the activity of pure SBA-15. Ion-exchangers are known to

6**at a catalyst loading of** 1.5 **wt% and** alcohol **to** lipid **ratio of 20** be reusable through regeneration with solutions containing the proper counter ions. The use of SBA normally required activation or regeneration by soaking or washing with sodium hydroxide solution. However, no explicit report of its reusability data and activity retention of regenerated resins have been reported after using them as a catalyst for the transesterification of RBL. Unlike ion-exchange resins which would need to be syn- thesized, zeolites could be sourced naturally and are consid- ered an abundant and low-cost resource [112]. Zeolites are formed by three-dimensional frameworks of aluminosilicate and are known to have a uniform porous structure having acidic sites [35, 112]. To use zeolites as a base catalyst for transesterification of RBL, they are modified by impregnation with K2CO3 [35] or KNO3 [112], and subsequently calcined. Compared to KNO3-modified zeolite, which can achieve a FAME yield of ~83% with

6**a catalyst loading of 10 wt% and methanol to** lipid **ratio of**

12 in 4 h [35], modification of zeolite with K2CO3 resulted in better yields (~98%), required lesser catalyst (4 wt%), lower methanol to lipid ratio of 10, and a shorter reaction time of 3 h [112]. The observed difference in the performance may be owing to the amount of potassium attached to the modified zeolite, with KNO3-modified zeolite reported to have ~4.8 wt% while K2CO3-modified zeolite having ~11.5 wt%. The extent of incorporating potassium may be influenced by the quality of the natural zeolite obtain- ed and the pretreatment and modification protocols adopted. Prolonged reaction time using K2CO3-modified zeolite was found to result in a decrease in BD yield and is attributed to the possible reversal of the reaction [112]. Despite the high yields achieved using K2CO3-modified zeolite under favor- able conditions, its reusability is not reported. Owing to concerns on renewability of the catalyst and re- lated raw materials, activated carbon, which could be derived from biomass, has also been used as catalyst support and ap- plied in the transesterification of RBL. Specifically, palm ker- nel shell was impregnated with 25 wt% of each of the two widely used base catalyst KOH and CaO

3**and calcined at 500 °C for 5 h**

to produce the desired activated carbon having a basic site of 1.86 mmol g−1 [113]. Despite the low basic sites as compared to potassium activated or doped transitions metals like ZnO and Al2O3, its performance as a catalyst is found to be comparable. Unfortunately, further comparisons could not be possible because there is no information regard- ing the textural properties, and the reusability of the catalyst was not investigated. Most recently, a novel catalyst devel- oped is an insoluble organo-nickle (0.5 wt% Ni-Schiff base chelate promoter with 1 wt% Ni(CH3COO)2·4H2O loading) material for transesterification under H2 atmosphere [114]. With the use of such catalyst, high yields of up to 93.5% could be achieved at 65 °

23**C for** 2 **h**, and **with a methanol to** RBO **ratio of**

6, which is comparable with homogeneous base catalyst. Biomass Conv. Bioref. However, after the 4th cycle of use, the yield dropped to less than 72%. The use of such catalyst is still in its developmental stage and requires multiple and long synthesis steps, without a specific reactivation process of deactivated catalyst as com- pared to metal oxides and anionic exchangers. Generally, metal oxides could be adopted as heterogeneous base catalyst, but would require impregnation of an active agent and/or activation at high temperatures of over 500 °C. In addition, these types of catalyst also suffer from deactiva- tion via contamination or blockage of active sites, and/or leaching of active sites, which would require reactivation or regeneration steps. Similar to their homogeneous counter- parts, heterogeneous base catalysts are mostly employed in the transesterification of refined or pretreated RBL with little to no FFA when possible. Contrary to most understanding that base catalyst could not be used in the esterification of FFA as it would end up in saponification, the main culprit that leads to such an undesirable reaction is the presence of water and is most evident with alkaline bases and at temperatures below the boiling point of water. The continuous removal of water allows the formation of esters from FFA and alcohol even with the use of a base catalyst [116–118]. Since most alcohols used such as those in BD production have boiling tempera- tures less than that of water, base catalyzed esterification with these alcohols is seldom or not explored at all. However, glyc- erol that is produced during the transesterification of AGs has a normal boiling point of ~290 °C, which could be recycled and used to reduce the FFA content of unrefined lipids to make it suitable for subsequent transesterification step. Zeng et al. [119], was able to successfully use 0.1%w/w ZnO as a catalyst in the esterification of FFA in RBL with glycerol

> 3**to reduce the acid value from** 38.14 **to** 5.17 mg·**g**

−1 after reacting for 6 h at 200 °C at a stoichiometric dosage of glycerol. Heterogeneous multi-step or simultaneous acid and/or base- catalyzed To carry out esterification of FFA at lower tempera- tures and adopt the use of short-chain alcohols, reactions are most widely carried out with the aid of an acid catalyst. Like that of their homogeneous counterparts, the transesterification activity of heterogeneous acid catalysts is lower compared to those of bases. These are best adopted for esterification, with the subsequent transesterification carried out either using homogenous [120] or heterogeneous [36, 110] base catalyst. However, the use of the heterogeneous acid catalyst for (trans)esterification has also been reported [121, 122]. Generally, acid catalysts could be classified into heteropoly acid derivatives [36, 123], cation exchanger [110], sulfonated carbon [122], zirconia-based or modified- zirconia [121], and sulfated metal [120]. In most cases, hetero- geneous acid or multi-step heterogeneous acid/base-catalyzed RBL transesterification typically requires a much longer time of over 8 h and higher alcohol to RBL molar ratio, as high as 15 to 40, and catalyst loading of 3 to over 100 times more than what is required for homogeneous acids. Heteropoly acid (HPA) derivatives, specifically Keggin- type HPA such as 12-tungstophosphoric acid (TPA, H3PW12O40) supported on an appropriate matrix, are explored in biodiesel production owing to their structural mobility and super acidity [115]. Silica impregnated with TPA (H3PW12O40/SiO2) [36] and cesium-exchanged or cesium salt of TPA (CsH2PW12O40) [123] have been used to esterify RB FFA. At 3 wt% loading, the use of H3PW12O40/SiO2 can reduce the FFA content of RBO from 11 wt% to less than 1.3 wt% in 2 h at 70 °

> 3**C with a methanol to oil molar ratio of** 10 [36]. In **the**

study conducted by Srilatha [123], CsH2PW12O40 loaded at 0.041 g per cm3 of the reaction mix- ture; a conversion of 92.4% could be achieved in 4.2 h

> 3**at 65 °C** at **methanol to** RB FFA **molar ratio of**

14. It was also indicated in their study that TPA exchanged with more Cs an acidity of 0.840×10−4 mol NH3 per g of catalyst, but its resulted in lower acidity, with CsH2PW12O40 reported to have catalytic activity decreases to ~77% on the 5th reuse. Cation exchanger DIANIONTM PK208LH (sulfonic acid functionalized styrene-divinylbenzene co-polymer) has also been explored but requires up to ~77 to 100 wt% of catalyst to significantly reduce the RBL with an FFA of 14 wt% to less than 2 wt% [110]. Another type of sulfur-containing acid cat- alyst is sulfated metal oxides [115]. Ferric sulfate (Fe2(SO4)3) [120] has also been used

> 14**to reduce the FFA content** in RBL **from** 22 **to**

~3%, at a catalyst loading of 3 wt% for 3 h, under continuous reflux with ethanol to RBO molar ratio of 8. The advantage provided by heterogeneous catalysts over homoge- neous catalysts in a multi-step (trans)esterification process is the possibility of directly feeding products from the esterifica- tion step into the subsequent transesterification process, with- out having to neutralize the acid used during esterification [36, 110, 120], but could be passed through silica gel or other water removing agent before transesterification [120]. Single-step (trans)esterification is also possible with the heterogeneous acid catalysts. The synthesis and use of chlorosulfonic acid modified-zirconia were explored by Zhang et al. [121]. In their research, it was observed that chlorosulfonic acid modified zirconia with a total acid site of 6.29 mmol·g−1 is found to be more active than sulfuric acid modified zirconia, while achieving 100% yield in FAME even at 40 wt% FFA content and initial water con- tent of up to 3 wt% and maintaining at least 92% of its catalytic activity after 3 cycles of use. However, the use of such a catalyst requires much higher temperatures of 120 °C, a longer reaction time of 12 h, and larger methanol to RBO molar ratio of 12. Sulfonic functionalized catalyst can also be derived with biomass-based carbon as support. Rice chaff or RB carbonized under 400 °C for 75 min was sulfonated by Fereidooni et al. [122] to serve as a hetero- geneous catalyst. Sulfonated carbonized RB at a loading of 1.5 wt% resulted in a FAME yield of up to 97% at a rela- tively lower

12**temperature of** 65 °**C and** a shorter **time of 6 h**

for a reaction carried out at methanol to RBO molar ratio of 10. Such catalytic activity is comparable with sulfuric acid as reported previously by Zullaikah et al. [30], but would require RBO to have an FFA content of >75 wt%. Unfortunately, the FFA content of the RBO (trans)esterified using sulfonated carbonized-RB carried out by Fereidooni et al. [122] was not indicated. This hin- ders an objective comparison and understanding of how such high yields could be effectively achieved. These types of catalysts require the impregnation of the catalyst sup- ports (Zr(OH)4 or carbonized biomass) with sulfonating agents (chlorosulfonic acid or sulfuric acid), and calcined or activated at elevated temperatures below boiling temper- atures of the activating agents [121, 122]. Heterogeneous acid catalysts adopted in the BD synthesis from RBL are very promising, but most of these catalysts do not have their reusability and regeneration processes reported. solvents. This also means that at least two types of solvents would be required in the conventional process of BD production from RB. An additional solvent like acetone may be employed if partial refining like degumming and dewaxing is required [30, 101]. The number of solvents used may be avoided through in situ (trans)esterification (ISTE), where the alkyl donor is at the same time serving as the extracting solvent in a single process. In a detailed review regarding ISTE by Go et al. [124], ISTE is defined as a process involving the (trans)esterification of lipids within the biomass matrix or as the lipids are being extracted, and the simultaneous extraction of products and/or lipid constituents without a distinction between extraction and reaction steps. In the same review for unit processes with a distinct extraction step and the conversion of lipids to BD occurring entirely outside of the biomass, this is further referred to as pseudo-ISTE or one-pot sequential extraction and (trans)esterification (OSETE). Adopting ISTE or OSETE for BD production from RB could eliminate various process steps like extraction and refining of 3.4.2 In situ (trans)esterification and one-pot sequential extraction and (trans)esterification lipids while maximizing the conversion of available FA into BD (Fig. 5b). Published research works on the catalyzed ISTE and OSETE of RBL are summarized and presented in Table 5. Industrial BD production largely adopts conventional processing of lipids that requires the pre-extraction and partial or complete refining of extracted lipids (Fig. 5a). As have been previously discussed, the effective extraction of RBL requires the use of In situ transesterification of RBL Like conventional BD syn- thesis, ISTE adopts the use of similar catalysts and solvents, where esterification and transesterification steps could either Conventional (Trans)esterification Solvent Recovered Solvent Rice Bran Stabilization & Pelletizing Extraction Catalysts 1 Residual Bran Solvent Recovery Wax & Gums Dewaxing / Degumming Dewaxed Recovered Recovered Degummed Rice Bran Oil Alkyl Donor Alkyl Donor Esterification Separation Trans esterification Separation / By- (Trans)esterification – Simultaneous Reaction Purification Products Glycerol Rice Bran Biodiesel Alkyl Alkyl Donor Donor Catalysts 2 Wastewater a In-situ (Trans)esterification (ISTE) Recovered Recovered Rice Bran

Alkyl Donor Alkyl Donor Biodiesel Rice Bran Esterification Separation Trans esterification Separation / By-(Trans)esterification – Simultaneous Reaction Purification Products Catalysts 1 Residual Bran Glycerol Rice Bran Alkyl Donor Enzymatic Hydrolysis Pretreatment Rice Bran Alkyl Donor Catalysts 2 Wastewater Residual Bran b Dillute Acid Hydrolysis Pretreatment Enzyme Hydrolysis Separation Drying Sulfuric Acid Hydrolysis Drying/ Separation Wet Hydrolyzed Carbonization/ Functionalized & Lipid-Dense Bran Sulfonation Residue Water Sugar-Rich Lipid-Dense Hydrolysate Hydrolyzed Bran Water Sugar-Rich Hydrolysate Extraction ISTE c Fig. 5 General process flow schemes of conventional (a),

18**in situ (trans)esterification** (b), **and** hydrolysis pretreatment **of**

rice bran (c). To be printed in black and white Table 5

18**In-situ (trans)esterification** and sequential **extraction and (trans)esterification**

of rice bran lipids with acid and/or base catalyst* Feedstock Quality a Alkyl Donor Solvent Loading b Catalyst Loading Mixing / Irradiation / Heating T (°C) / P (MPa) / t (h) c Space Loading / Yields and Purity e Ref. (cm3/g) b and Co-solvent Reactor Loading d M: 12 L: 19 F: 19 / 68 P: n.s. f M: 12 L: 19 F: 19 / 60 P: n.s. M: n.s. L: n.s. F: 13 /48 P: n.s M: 4 L: 17 F: 3 P: n.s. M: 4 L: 17 F: 3 / 30 P: n.s. M: L: F: P: M: L: F: P: 4. 14 24 n.s. 9 19 80 < 1.40 M: L: F: P: 9 19 80 < 1.40 M: n.s. L:

2**n.s. F: n.s**. P: **n.s. Methanol**

: 4 Ethanol: (96%) 4 Methanol: 10 Methanol: 15 Step 1 Methanol: Step 2 Methanol SLRn: SLR: SSR: SLRn: SLR: SSR: SLRn: SLR: SSR: SLRn: SLR: SSR: SLRn: 15 SLR: SSR: 8 Methanol: 5 Methanol: 1.5 Pet. Ether 3 Step 2 Methanol 0.3 Ethanol: Pet. Ether Step 2 Ethanol 1.5 3 0.8 Methanol 15 - g ~21* 4 - ~21* 4 - - 10 - ~88* 15 - ~141 24 SLRn: - SLR: ~36* SSR: 5 SLRn: SLR: SSR: - ~25* 4.8 SLRn: SLR: SSR: - ~28* 5.3 SLRn: SLR: SSR: - - 15 H_2SO_4 Magnetic Stirrer 2.5 vol.% of methanol Mixing speed not specified 18.4 wt.% of the solid* Heating not specified H_2SO_4 Magnetic Stirrer 3.75 vol.% of ethanol Mixing speed not specified 27.6 wt.% of the solid* Heating not specified H_2SO_4 Ultrasonic Water Bath 1.5 vol.% of methanol 35 kHz, 500 W 27.6 wt.% of the solid H_2SO_4 Magnetic Stirrer 1.0 vol.% of methanol* 600 RPM 27.6 wt.% of the solid Hotplate Water Bath Step 1: Magnetic Stirrer H_2SO_4 600 RPM 27.6 wt.% of the solid Hotplate Water Bath Step 2: NaOH 8 N in Methanol H_2SO_4 Magnetic Stirrer 1.5 vol.% of methanol 600 RPM 13.8 wt.% of solid* Hotplate Water Bath Step 1: Mechanical Stirrer H_2SO_4 Mixing speed not specified 1.5 wt.% of the solid Soxhlet Apparatus Step 2: NaOH 1.4 wt.% of the solid Step 1: Mechanical Stirrer H_2SO_4 Mixing speed not specified 1.5 wt.% of the solid Soxhlet Apparatus Step 2: NaOH 1.4 wt.% of the solid H_2SO_4 Magnetic Stirrer 1.84 wt.% of the solid* Mixing speed not specified or Soxhlet Apparatus 9.2 wt.% of the solid* T: ~64* P: Ambient t: 1 T: ~78* P: Ambient t: 1 T: 60 P: Ambient t: 4 T: 60 P: Ambient t: 4 T: 60 P: Ambient t: 0.25 + 1 T: 60 P: Ambient t: 1 T: P: t: - Ambient 3 + 3.5 T: P: t: - Ambient 5 + 3.5 T: 68 P: Ambient t: 5 SL: RL: - - SL: RL: - - SL: RL: 25* ~45* SL: RL: 25* ~65* SL: RL: 25* ~68* SL: RL: 25* ~24* SL: RL: - - SL: RL: - - SL: RL: - - YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: YS: YL: YP: CAE: - - 24 / 86 - - - 84/98 - - - 75 / 83 71 / 82 - - 75 90 - - 97 95 - - 50 97 16.7 ~88* ~95 - 16 ~84* ~96* - 18 / 17 - - 67 / 75 [29] [29] [127] [128] [128] [19] [32] [129] [130, 131] * Entries to the table are calculated based on available information to facilitate comparison; a Rice bran quality in terms of moisture content (M, wt.%), lipid content (L, wt.%), free fatty acid content (F, to mass ratio (SLR, cm3 /g), and solvent-to-solid volume to dry biomass ratio (SSR, cm3 /g); c Temperature (T), pressure (P), and time (t); d

2**Space loading** (expressed **as the reactor volume to the amount of**

wt.%), and particle size (P, mm); b Alkyl donor and co-solvent relative to the mass of dry solid (cm3 /g), solvent loading as expressed in terms of solvent-to-lipid molar ratio (SLRn), solvent-to-lipid volume biomass loaded, cm3 /g), and reactor loading (percentage of the reactor volume occupied by the reaction mixture); e Yields expressed as the amount of FAAE relative to the solid (YS), relative to the total lipids (YL), and relative to the theoretical maximum amount of alkyl ester (YP), with purity (CAE) expressed as the alkyl ester content; f not specified (n.s.); g incomplete information to allow estimation Biomass Conv. Bioref. be done simultaneously or sequentially. The ISTE of RBL was introduced by Özgül-Yücel and Türkay [29, 125, 126] in their series of works published between 1993 and 2003. The use of methanol was found to be most reactive and effec- tive in the in situ esterification of high acid value RBL when compared with other monohydroxyl alcohols [125]. The use of methanol was recommended for the in situ process to de- acidify high acid value RBL owing to its selectivity for FFA extraction over triglycerides, leaving all triglycerides in the RB and obtaining products having higher purity of desired esters [29]. It was also found that 5 cm3 of H2SO4 per 50 grams of RB or ~18.4 wt% of acid relative to RB was most suitable, to avoid alteration of the bran and obtaining a resid- ual bran with increased stickiness that hinders separation [126]. From the same study, it was observed that increasing from 20 to 65 °C improved FAME yield, while moisture con- tents from 2 to 13 wt% in RB and an SSR from 4 to 5 cm3·g−1 found to have minimal influence on the yield and ester content in the product. However, higher SSR resulted in lesser resid- ual lipids in the RB processed. Apart from esterification, transesterification could also occur as some of the acylglycerides are extracted during the in situ process. Rice bran with lipids of higher acid value was more easily convert- ed to alkyl esters as compared to those with lower acidity (Table 3) for acid-catalyzed in situ (trans)esterification. However, the use of ethanol greatly improves the conversion (> 90%) of lipids to esters as compared to methanol with conversions ranging only from 24 to 86% for RB having lipids with FFA content from 19 to 68 wt%, but would require higher acid loading of up to 27.6 wt% of RB (7.5 cm3 H2SO4 per 50 g of RB) [29]. Adopting the same concept and taking advantage of methanol’s selectivity, Gunawan et al. [19] later in 2011 optimized the process with RB con- taining ~24 wt% FFA and using methanol

9**at an SSR of** 5 cm3·**g**−1 **at** 60 °**C with**

a catalyst (H2SO4) loading of 27.6 wt% of RB for 1 h, to produce products with high FAME content (~97%), but low FAME yield of ~50% relative to the potential maximum FAME. In 2009, Yustianingsih et al. [127] adopted the use of indi- rect ultrasonication during the ISTE of RBL, with methanol as the alkyl donor

9**at an SSR of** 10 cm3·**g**−1 **at** 60 °**C with**

a catalyst (H2SO4) loading of 27.6 wt% of RB for 4 h, to achieve a reaction yield of 75 to 83% for RB with lipids containing 14 to 48 wt% FFA. Ultrasonication at a constant temperature only improved the initial reaction rate but did not improve the final yields and conversions of the RBL in an ISTE process. The use of an acid catalyst such as H2SO4 in conventional BD synthesis was best adopted for esterification, with transesterification typically requiring more alcohol and prolonged reaction time. However, for RB with lipids contain- ing 3 wt% FFA with methanol as the alkyl donor, an ISTE reaction yield of only 75% could be achieved, with a FAME content of ~90% even

9**at a** higher **SSR of** 15 cm3·**g**−1 **at** 60 °**C** with **a** catalyst (H2SO4) loading of 27.6 wt% of RB for 4 h [128]. Although acid-catalyzed ISTE of RBL could achieve products with high FAME contents, the available fatty acids are not effectively and efficiently converted and recovered. To improve the overall process yield of ISTE of RBL, Shiu et al. [128] proposed a

2**two-step acid-base catalyzed ISTE**

. The proposed approach involved the reaction being carried out for 15 min at 60 °C with an acid-catalyzed process (SSR = 15 cm3·g−

13**1 and catalyst** (H2SO4) **loading of** 27.6 **wt**

% of RB) to reduce the

24**FFA content to less than** 1 **wt**% and **the** subsequent addition **of**

excess alkaline methanol (8-M NaOH) at 8 cm3·g−1 RB and allowed the reaction to proceed for an hour. The excess amount of base added is to facilitate neutralization and the remaining as a catalyst. The proposed approach was found to achieve high reaction yields of 97% and products having FAME content of over 95%. The said process has been tested to be applicable for RB containing FFA from 3 to 30 wt%. Compared to conventional acid-base catalyzed se- quential esterification and transesterification, the

2**two-step acid-base catalyzed ISTE**

avoids the separation of metha- nol and removal of water generated after the esterification step. Although not explicitly indicated, the influence of water generated from the esterification step on the later transesterification step may have been reduced owing to the large excess of methanol present and the presence of Na2SO4 and rice bran matrix, which could dilute and ab- sorb the water generated, respectively. The use of such a process requires large quantities of methanol with an over- all SSR of 24 cm3·g−1 RB. However, Shiu et al. [128] have argued that methanol could easily be separated and recov- ered from the products with the co-generation of a useful by-product Na2SO4. In addition, adopting such process was also later found to enable the co-extraction of oryzanol, which was found in the final product mixture [14]. One-pot sequential extraction and (trans)esterification of RBL Over the years, some variations of the ISTE have been proposed. In view of catalyzed processing of RBL, two research groups led by Xuefeng Ding [32, 129] and Sitti Zullaikah [130, 131] explored the use of a Soxhlet extrac- tor to carry out the apparent in situ process. In the attempt made by Lei et al. [32, 129], they explored the use of methanol and ethanol to process RB with lipids having an FFA content of up to 80%. The reactions were carried out with RB packed in a Soxhlet extractor and while meth- anol acidified with H2SO4 placed in the distillation flask as the extraction and reaction commenced under continuous reflux, overall (trans)esterification reaction yields achieved were ~88% after 5 h for methanol [32] and ~93% for eth- anol after 7 h [129] at an acid loading of ~ 1.5 wt% of the RB or ~7.9 wt% relative to the available lipids. In the work of Zullaikah et al. [130] and Yasmin et al. [131], even with a larger excess in methanol at an SSR of 15, from ~ 1.84 wt% of the RB to ~9.2 wt% only improved the FAME content in the product from 67 to 75%. Although the FAME yields expressed relative to the amount of RB processed were reported to be ~17% in both works by Zullaikah's group [130, 131], it cannot be verified whether the available fatty acids were completely converted or not, since the lipid content and initial FFA content were not reported. However, in the works reported by Xuefeng Ding's group [32, 129], they have noticed that alcohols have relatively poor extracting power and the addition of petroleum ether as a co-solvent at an alcohol to petroleum ether volume ratio of 0.5 and an overall SSR of ~5 cm3·g−1 RB allowed the complete extraction of the extractable lipids, but at the expense of lesser extent of conversion of the available acylglycerides. To complete the reaction, Lei et al. [32, 129] introduced alcohols containing NaOH di- rectly to the extracted and pre-esterified lipids to neutralize the available acids and with the excess base catalyzing the transesterification reaction to achieve an overall reaction yield or conversion of over 95% after a total reaction time of 6.5 h and 8.5 h for methanol and ethanol, respectively. To facilitate the removal of water from neutralization and the esterification step, the same researchers replaced the RB-packed extractor with one packed with CaO. Furthermore, the researchers reported that the CaO served not only as a desiccant, but could also be further converted into micro-/nanostructured rod-shaped CaCO3 via carbon- ation, as a value-added product. Even though most re- searchers claimed that the process was partly in situ, this may not be the case because the extraction and reaction steps are actually occurring in different chambers of the single equipment setup, and given that the boiling point of sulfuric acid is over 250 °C, it is unlikely to be evapo- rated along with the alcohol. Thus, these processes are in principle sequential extraction and transesterification of RBL, which may be considered an OSETE. Another point of consideration when using a Soxhlet extractor is the ac- tual reaction temperature. The extraction may be occurring near the boiling point of the solvent or alkyl donor used but the (trans)esterification may be happening at a much higher (>100 °C) temperature if a heating mantle was used instead of a temperature-controlled heating bath, owing to higher boiling points of the ester and solvent mixture. Provided that proper optimization of a true ISTE or an OSETE is done, it could potentially reduce processing time, required processing steps, and overall solvent requirements, with its main challenge being the use of high catalyst loading. 3.4.3 Supercritical and subcritical solvent (trans)esterif ication One common and consistent endeavor in the development of the biodiesel production process is the minimization of catalyst required, ease of catalyst separation, and minimized usage of solvent. These could not be achieved all at the same time and without certain compromise, but there are develop- ments with favorable outcomes. The use of alkyl donors under subcritical or supercritical conditions has been explored in the recent 2 decades. Subcritical conditions are temperature and pressure conditions above the normal boiling point of the ma- terial but below its critical point, while supercritical conditions are temperature and pressure combinations above the critical conditions. For reactive systems such as those in biodiesel synthesis, the presence of lipids and other reaction compo- nents also influence the required temperature and pressure to achieve sub- or supercritical reaction conditions [124]. Supercritical transesterification was explored much earlier and

23**was pioneered by Saka and Kusdiana** [132] **in 2001**

. The successful synthesis of biodiesel with rapeseed and su- percritical methanol by Saka and Kusdiana [132] led to vari- ous developments in supercritical (trans)esterification using various alcohols [133], alkyl carboxylates [134, 135], and dimethyl carbonate [136]. Further developments included the 2-step processes involving hydrolysis [137, 138] or acidolysis [139] with acetic acid under subcritical conditions and subsequent esterification under supercritical conditions to reduce the severity of reaction conditions. These develop- ments initiated by Shiro Saka’s group spanned from 2001 to 2012. Although subcritical (trans)esterification conditions have also been explored around the same time, it was in 2013 when catalyst-free (trans)esterification was reported to be possible under such condition by Ju et al. [140]. Additional developments on subcritical (trans)esterification conditions involving the exploration of catalytic activities of water [141] and acetic acid [142] under such conditions, specifically their application in ISTE [143–147], were initiated by Yi-Hsu Ju’s groups from 2012 to 2019. (Trans)esterification under supercritical conditions is often criticized for its high- temperature requirement of over 270 °C, while subcritical conditions suffer from the requirement of high solvent-to- lipid ratio (SLR) [124]. However, under these conditions, the use of conventional catalysts could be avoided, and the reaction inhibition by the presence of water and/or FFA is of lesser concern. The conversion of RBL to biodiesel under sub- and supercritical conditions has also been explored by differ- ent researchers (Table 6) from 2009 onwards. Supercritical (trans)esterification of RBL The (trans)esterification of DDRBO was investigated 8 years after the introduction of supercritical (trans)esterification technolo- gy. In the work of Kasim et al. [148], a reaction yield of ~95% was achieved in 5

3**min at** 300 °**C with methanol to oil molar ratio of**

271 and pressurized with CO2 to a pressure of 30 MPa. Although high yields could be achieved, it was also noted that the final product contains only about 89.5% FAME with ~3% hydrocarbons resulting from the decomposition of AGs. The Table 6 Conventional and

18**in-situ (trans)esterification of rice bran**

lipids under sub- and supercritical solvent conditions* Feedstock Quality

2**a Alkyl Donor and Co-solvent** (cm3/g) **b** Solvent Loading b **Catalyst**

Loading Mixing / Irradiation / Heating

2**T (°C) / P (MPa) / t (h**

) c Space Loading / Reactor Loading d Yields and Purity e Ref M: L: n.a. f n.s. f F: 12.3 P: M: n.s. L: 17.4 F: 12.3 P: n.s. f M: 10.2 L: 18 F: 18 - 80 P: n.s. M: 4 L: 41.4 F: 32.9 P: n.s. M: 8.7 L: 48.41 F: n.s. P: n.s. M: 13 L:

2**n.s. F**: 37 P: **n.s. M: n.s**

. L: 11.8 F: 40.4 P: n.s. M: n.s. L: 15.5 F: 63.5 P:

5**n.s**. M: **n.s**. L: **n.s**. F: **n.s**. P: **n.s**

. Methanol: CO2: Methanol: CO2: Methanol: CO2: Acetic Acid: Methanol: Methanol: Methanol: CO2: Water: Methanol: CO2: Water: Ethanol: CO2: Water: Ethyl Acetate: Methanol: CO2: Water: n.a. - SLRn: SLR: SSR: 2* - SLRn: SLR: SSR: 4.8 SLRn: - SLR: 1.2 SSR: 5 SLRn: SLR: SSR: 5 SLRn: SLR: SSR: 6 SLRn: - SLR: 2 SSR: 4 SLRn: - SLR: 4 SSR: 6.4 - 1.6 2 - SLRn: SLR: SSR: SLRn: SLR: SSR: 271 11.5 n.a. 271 11.5 ~2* - ~33* 6 - ~12* 5 - ~10* 5 - ~8* - ~34* ~8* - 64.5* ~10* - - No catalyst was used n.s. No catalyst was used n.s. Acetic Acid No mixing 25 vol.% of methanol Electric Resistive-Heating 126 wt.% of solid* Heating at 5 °C/min Sulfonic Sites 1.1 mmol/g solid Sulfonic Sites 1.6 mmol/g solid No mixing Electric Resistive-Heating Heating at 4 °C/min No mixing Electric Resistive-Heating Heating at 5 °C/min No catalyst was used No mixing n.s. No catalyst was used No mixing n.s. No catalyst was used No mixing Electric Resistive-Heating Heating at 10 °C/min No catalyst was used No mixing Electric Resistive-Heating T: 300 P: 30 t: ~0.083 T: 300 P: 30 t: ~0.083 T: 250 P: 12 t: 1 (1.75) h T: 185 P: 2.5 t: 0 (0.55) T: 165 P: 1.6 t: 0 (0.45) T: 200 P: 4 t: 3 T: 200 P: 10 t: 3 T: 160 P: 8 t: 2 T: 200 P: 4 t: 7 SL: RL: -g - SL: RL: - - SL: RL: - - SL: RL: ~12* 66 SL: RL: ~12* 61 SL: RL: ~17* ~82* SL: RL: ~17* ~82* SL: RL: ~30* ~37* SL: RL: - - YL: - YP: 94.8 CAE: 89.5 YS: - YL: - YP: 51.3 CAE: 52.5 YS: 15.5 YL: 85 YP: 99 CAE: - YS: 36.3 YL: 87.8 YP: 94.8 CAE: - YS: 43.5 YL: 89.9 YP: 98 CAE: - YS: - YL: 65.2 YP: - CAE: 73.5 YS: - YL: 98 YP: - CAE: 83.9 YS: - YL: - YP: 79.8 CAE:

60.6 YS: - YL: ~80 YP: - CAE: - [148] [148] [14] [15] [16] [31, 53] [152] [151] [154] * Entries to the table are calculated based on available information to facilitate comparison; a Rice bran quality in terms of moisture content (M, wt.%), lipid content (L, wt.%), free fatty acid content (F, to mass ratio (SLR, cm3 /g), and solvent-to-solid volume to dry biomass ratio (SSR, cm3 /g); c Temperature (T), pressure (P), and time (t); d

2**Space loading** (expressed **as the reactor volume to the amount of**

wt.%), and particle size (P, mm); b Alkyl donor and co-solvent relative to the mass of dry solid (cm3 /g), solvent loading as expressed in terms of solvent-to-lipid molar ratio (SLRn), solvent-to-lipid volume biomass loaded, cm3 /g), and reactor loading (percentage of the reactor volume occupied by the reaction mixture); e Yields expressed as the amount of FAAE with respect to the solid (YS), with respect to the total lipids (YL), and with respect to the theoretical maximum amount of alkyl ester (YP), with purity (CAE) expressed as the alkyl ester content; f not specified (n.s.) and not applicable (n.a.); g incomplete information to allow estimation; h total time including heating Biomass Conv. Bioref. amount of methanol used in the (trans)esterification of DDRBO is much higher than what is typically required for supercritical methanol (trans)esterification, which is only about 40 [132]. The use of high amounts of methanol was to enable comparison with supercritical methanol ISTE of BRL, which could be considered an early attempt to adopt supercrit- ical methanol in ISTE. Unfortunately, adopting ISTE under supercritical methanol conditions for RBL only allowed a re- action yield of ~51% [148]. The low yield was attributed to degradation and other side reactions of the raw material with part of the bran matrix being liquefied and/or carbonized. Apart from methanol, ethanol has also been used in super- critical (trans)esterification of refined RBO (RRBO) [149] and RBO fatty acid distillate (RBOFAD) [150]. Vieitez et al. [149] carried out supercritical ethanol (trans)esterification of RBO using a 39-cm3 tubular reactor with ethanol to total fatty acid molar ratio of 40:3, 350 °C, and 20 MPa, over a wide range of flow rates (0.8–2.5 cm3·min−1) and at different FFA content (0–100 wt%). The authors observed that lower flow rates re- sulted in higher FAEE in the product, but higher flow rates resulted in lower decomposition. Likewise, the presence of FFA avoids decomposition and required shorter residence time. The addition of FFA effectively reduced the amount of glycerol in the system which promoted several side reactions under such condition, where the authors have indicated that a decrease in the degree of decomposition from as high as 16% to less than 5% was observed as FFA content was increased from 0 to 100 wt%. Moreover, RRBO required a residence time of 39 min to achieve high FAEE content of ~75%, while RBO with FFA over 50 wt% required 16–26 min to achieve an FAEE content of ~95%. These findings are favorable in the actual use of RBL because RBL tends to have high FFA owing to the hydrolytic activity of indigenous lipases as pre- viously discussed. Moreover, an extension to its applicability is the use of fatty acid distillate (FAD) produced during the refining of RBL. Akkarawatkoosith et al. [150] explored the use of RBOFAD which contained 65.5 wt% FFA for (trans)esterification with ethanol at an ethanol to oil molar ratio of 5 in a microreactor at 300 °C and 8.5 MPa over a residence time of 24 min. The FAEE content under the local optimum condition was only 75%, which does not meet stan- dard requirements of ≥96.5 wt% of alkyl ester. In the same study, reaction additives or auxiliaries such as iso-propanol and acetic acid were also explored but were not effective in improving the biodiesel content (

24**ester content) in the product. The** decrease in FAEE **content** upon **the**

addition of iso- propanol and acetic acid was attributed by the authors as a result of dilution, either slowing down the reaction process and/or formation of other products apart from FAAE. Thus, ester content or purity should not be the only response con- sidered but should also account for the actual process yield and conversion, to elucidate the influence of such additives/ auxiliaries. Nevertheless, the results of these studies provide possibilities of converting RBL to BD without the need for a catalyst. Subcritical (trans)esterification of RBL The catalyst-free (trans)esterification of pre-extracted RBL under subcritical conditions is less explored. This is probably owing to the high requirements of alcohol and long reaction time required if no catalyst is employed. However, adopting the use of alcohols under subcritical conditions in ISTE may be a good way to take advantage of the excess alcohols and address the inherent drawbacks in (trans)esterification of pre-extracted RBL under subcritical conditions. Two research groups led by Yi-Hsu Ju [14–16, 31] and Sitti Zullaikah [31, 130, 151–153] have ex- plored this possibility in about the same time from 2014 and onwards (Table 6). Acting as a solvent and as a catalyst, acetic acid was added along with methanol to decrease the overall solvent require- ment to as low as 6 cm3·g−1 and the temperature to 250 °C, while achieving a yield of ~15.5 g of FAME per 100 gram of RB processed, which is equivalent to a conversion of ~99% [14]. However, such high conversion was only achieved by pressurizing the system with CO2. Reactions carried out under nitrogen atmosphere only

19**achieved a FAME yield of** ~67.4 **g** per 100 **g** of RB. **In**

addition, oryzanol was also co-extracted during the ISTE of RBL under subcritical condition, with systems pressurized with CO2 resulting in higher recovery of oryzanol (~143%) than those pressurized with N2 (~90%) [14]. The presence of carbon dioxide under supercritical con- ditions may have served as co-solvent, which aided the extrac- tion process and the reaction process. Zullaikah's group on several occasions improved the FAME yield through the ad- dition of CO2 [31, 151–153] with systems pressurized up to 10 MPa resulted in high yields of up to 98%, relative to the extractable RBL [152]. Also, the presence or addition of water was found to be an effective way to reduce reaction severity, allowing high reaction yields to be achieved at lower temper- atures of 200 °C with a reaction time between 3 and 7 h [31, 151–154]. The addition of water during ISTE under subcritical condi- tions was also found to co-hydrolyze sugars found in RB, but the resulting hydrolysate only had sugar concentrations of less than 1 g·L−1 [31]. Separate works under the group of Yi-Hsu Ju reported a novel two-step process, with the first step adopting dilute acid hydrolysis to generate sugar-rich hydro- lysates (40 to 50 g/L) and lipid dense post-hydrolyzed RB (PHRB) containing ~40 to 50 wt%, and the subsequent (trans)esterification of the PHRB as the second step [15, 16]. Owing to sulfonation occurring during the drying of PHRB, the resulting PHRB was found in their study to be functional- ized with sulfonic acid groups which enabled high yields and conversions (> 95%) to be achieved in ~0.5 h with an SSR of as low as 5 cm3·g−1 and through non-isothermal ISTE from 30 to 185 °C at a heating rate of 4 to 5 °C·min−1. Although the (trans)esterification of RBL under subcritical conditions may be most suited only for ISTE, it provides a good balance between the severity of process conditions, while avoiding limitations brought about by the presence of FFA [14] and water [31]. Furthermore, bulk auxiliaries used under such conditions, including acetic acid, water, and CO2, could easily be separated and reused. Despite favorable yields and/or conversions having been reported, both sub- and su- percritical synthesis of BD from RBL face a challenge in producing a final product of high purity (>96.5%) to meet current standards. This is owing to the formation of degrada- tion products or by-products or the co-extraction of other com- ponents in RB during ISTE. These may cause hindrance in the subsequent direct use of the product but could also be lever- aged to co-produce by-products of high value. Future devel- opments may have to take these into considerations. 3.5 Factors affecting the productivity of biodiesel production from rice bran lipids Various processes could be adopted to produce BD from RBL, each having their advantage and disadvantage. Although attempts have been made to make comparisons be- tween processes under similar process conditions, these may to some extent have certain biases. Other constraints that are unique to the intended locality where the process will be im- plemented may also have to be considered. Instead, it would be important to understand the different factors influencing the different processes to better maximize and take advantage of the process adopted. Apart from the quality of RBL and the catalyst type of choice, which both greatly influence the re- quired processing or reaction time, there are other process variables or factors that can affect the actual process produc- tivity. In the following sections, the different factors affecting the productivity of biodiesel production from RBL will be elucidated, based on published works dealing with the con- version of RBL to BD. It should however be noted that most of these identified factors, if not all, are to some extent inter- dependent and are influenced by one another. Also, produc- tivity in biodiesel production should not only be concerned with the fraction of reactants converted to the desired product and the reaction time but should also account for the optimal use of process equipment and resources. 3.5.1 Mixing, temperature, and irradiation Mixing and agitation In any reaction system, the contact or collision between the reacting species is important as this would increase the probability of reaction to occur and keep the required reaction time to a minimum. Considering that RBL, which is primarily AG, has limited solubility in metha- nol, its mixing characteristics are important to ensure good contact and dispersion of one phase in another, whereby maximizing the interfacial area of contact [34]. Although var- ious studies on the (trans)esterification of RBL have looked into the influences of varying agitation speed [34, 155, 156], no consensus could be made regarding desired mixing char- acteristics that should be achieved apart from the fact that a well-dispersed system is desirable. For instance, Arora et al. [156] found that an agitation speed beyond 500 rpm did not further influence the degree of conversion during the esterifi- cation of RBL

19**with an acid value of** 24 **mg KOH·g**−1 **oil, with methanol**

as alkyl donor,

7**using sulfuric acid as catalyst**, and carried out **in**

a 500-cm3 reactor and agitated with a 1-inch magnetic stir bar. Using heterogeneous catalyst (CaO) in the transesterification of RRBO with ethanol in a 1-L reactor with a propeller-type agitator, it was observed by Sreedhar and Kishan [155] that an optimum agitation speed of 600 rpm was required to achieve high conversion (>70%), and higher agitation speed resulted in lower conversions (<55%). The said decrease was attributed to the observed formation of a vortex during mixing that resulted in the segregation of the reactants and the catalysts and was more evident at higher catalyst load- ing. Lakshmi et al. [34] carried out a separate and much de- tailed work on the mixing characteristics, providing details on the geometry of the reactor system involving a 1-L reactor equipped with a 4-bladed flat turbine and operating at 60% of the reactor capacity, where it was found that the critical agitation speed of 750 rpm was required for a non-reacting system and 700 rpm was required for a reacting system. It was also observed that systems having high FFA may actu- ally require lower agitation speed, but in any case, would require the mixing conditions to be either at the transition or turbulent regimes. The difficulty in coming up with a generalized mixing requirement is the lack of empirical information and is further complicated by factors includ- ing the quality and composition of RBL, the type and amount of alkyl donor and catalyst loaded, the mutual solubility of reactants, and the physicochemical properties (density, viscosity, and hydrodynamic diameter) of the reaction mixture, as well as the geometrical consideration of reactor system involved. Temperature and heating rate Another means of increasing the probability of collisions between reacting molecules is increasing the reaction temperature. This results in the lower- ing of viscosity, improved solubility, increase molecular vi- bration/ionization/protonation [121], or the combination thereof, thus resulting in improved reaction rates, which sub- sequently shorten the reaction time [88, 156, 157] and could even end up not requiring a catalyst [148–150]. The improved reaction rate due to the increase in reaction temperature also induces the shift in reaction equilibrium [46, 88], generally favoring the forward reaction, given that one of the reactants (alkyl donor) is often provided in excess. The reaction tem- perature for BD production can generally be divided into 3 regimes (Tables 3, 4, 5, and 6), from ambient conditions to the mixture's normal boiling point, subcritical conditions (normal boiling point to critical point), and supercritical conditions (above the critical point). In most cases, these conditions are based on the properties of the alkyl donor rather than the reaction mixture, which may be different from the actual con- dition of the reaction system, and thus presenting a grey area in defining the boundary of these regimes [124, 142]. Because reaction rates are improved at higher temperatures, less cata- lyst dosage or activity is typically required, and lower alkyl donor or solvent loading as reaction temperature is increased. Although higher temperature favors the reaction, it also leads to unwanted side reactions such as saponification for base- catalyzed reactions [46, 50], and potential decomposition at temperatures of 300 °C or higher, with the presence of glyc- erol and other materials possibly hastening the degradation process [148, 149]. For lipase-catalyzed (trans)esterification, the temperature may have to be kept at an optimum (30 to 50 °C) depending on the lipase used (Tables 3 and 4), to ensure that the lipases are most active while avoiding deactivation [47, 100, 102, 103]. Another factor seldom discussed in con- ventional (trans)esterification or reactions not carried out un- der sub- and supercritical regimes is the heating rate, which also requires careful assessment. For (trans)esterification car- ried out in batch reactors under sub- and supercritical condi- tions [142], and for ISTE, reaction and extraction could occur during heating [15, 16], even without the presence of a catalyst. Irradiation and intensity Other means of inducing mixing and increase in temperature involve the exposure of the reaction system to ultrasound and/or microwave irradiation. Ultrasound irradiation is the exposure of the reaction system to sound waves above 20 kHz up to 10 MHz. Electrical energy is transformed into heat and vibrational energy by an ultrasonic inducer, where the vibrational energy is in turn transformed into cavitation energy, which, upon release by the collapse of cav- ities generated during irradiation, results in localized heating, induced pressure, and improved heat and mass transfer of the reactants [158]. As for microwaves, these are electromagnetic waves with frequencies from 0.3 to 300 GHz. Microwave irra- diation results in high temperatures and pressure gradients with- in the system as a result of localized superheating via dipolar rotation and ionic conduction [157]. The localized superheating contributes to the thermal effects of microwaves, whereby im- proving the reaction rate and reducing the reaction time. However, microwave irradiation is also said to have non- thermal effects, although still not in consensus to its existence, which in some instances found to influence the activation en- ergy of the reaction [159]. Extensive reviews on the application of ultrasonic [158] and microwave [159] irradiation in the syn- thesis or production of biodiesel have been published in 2017 and 2019, respectively. In view of their application in BD production from RBL, it could be observed from Table 3 that compared to other conventional BD synthesis, ultrasound and microwave-assisted reactions required lower catalyst loading (< 1 wt%), and shorter reaction times (< 0.8 h) [157, 160, 161]. But unlike ultrasound-assisted reaction which has been adopted in ISTE [127], microwave irradiation has so far been only adopted in conventional (trans)esterification, which is found to be applicable for both closed [157] and open systems [160]. This may be because microwaves are less efficient when applied to systems containing solids [159]. Both ultrasound and microwave irradiation are said to be energy efficient owing to the mechanisms by which the energy is transferred to the reacting medium or species, minimizing unwanted heat loss through conduction and convection [158, 159]. Currently, these technologies are only done on a lab-scale and would be difficult to scale-up. In most studies reported, only the frequencies and power ratings are indicated. However, it is of importance during scale-up to maintain the effective and specific intensities of the irradiation applied to achieve the same performance. How these intensities could be expressed may vary from one system to another, as the quantity and type of material being exposed to, the area of exposure, and the geometry and position of the irradiation source may have to be taken into consideration. 3.5.2 Alkyl donor, co-solvents, and/or co-reactants Like mixing, temperature, and irradiation, the addition of ex- cess alkyl donors and co-solvents could shorten the reaction time by improving contact between reactants and shift the reaction equilibrium to achieve higher conversions or yields. However, excessive amounts of these materials in the system may result in lower productivity owing to a reduction in reac- tion rates, deactivation of certain catalysts, lesser amounts of lipids processed for a given reactor volume, and difficulties in product separation during downstream processing. Uniquely for biodiesel synthesis or production, the alkyl donor itself serves as the solvent for the reaction system, while other sol- vents added may be considered as co-solvents or co-reactants. Although there are different alkyl donors and co-solvents that have been explored for BD production, the discussions in this section will focus on those having been adopted for the pro- cessing of RBL. Alkyl donors Short-chain alcohols are the most explored alkyl donor for BD production and are so far the only group of donors adopted in converting RBL to DB. These short-chain alcohols generally ranged from 1 to 4 carbons [88, 102, 150] or, rarely 5 carbons, such as n-pentanol claimed to have been used in a certain patent [162]. Although the use of other alkyl donors other than alcohols is possible, these have not been widely adopted or explored in converting RBL to BD and are discussed in a later section (Section 3.6.2). In view of alcohols, longer chain alcohols have better miscibility or capacity to dissolve lipids but would tend to have higher vis- cosity and lower reactivity at a given temperature [29, 88]. Although methanol generally has higher reactivity than ethanol, when these are compared at temperatures near their boiling points, the yields are comparable with less alkyl donor required in the case of ethanol [90]. However, for lipase- catalyzed transesterification of RBL with alcohols, lipases tend to have affinity or preference for certain alcohols, with Novozym® 435 having better activity with methanol and ethanol, Lipozyme® TL-IM having a preference for

16**ethanol, n- propanol, and n-butanol**

, and Lipozyme® RM-IM having an affinity for

16**n-propanol and n-butanol**, as observed in **the**

study by Rodriguez et al. [102]. Among the different alcohols and alkyl donors, methanol and ethanol are the most widely explored or adopted alkyl donor in converting RBL to BD, with (trans)esterification with methanol generally requiring shorter reaction time (Tables 3, 4, 5, and 6). Co-solvents and co-reactants Apart from increasing the chain length of the alkyl donor, co-solvents have also been employed to improve mutual miscibility between reactants to reduce mass transfer. In the conversion of RBL to BD, the use of co-solvent is more prominent in ISTE, and OSETE, as co-solvents also improve the extraction rate apart from improving solubility [14, 32, 129]. Strict co-solvents do not get involved in the reaction itself; however, there are solvents which do not only improve mutual solubility between the reactant and extractability of the lipids but also take part in the reactions, which may be directly or indirectly involved to produce FAAE [14, 31, 151]. Several co-solvents, which include n-hexane [101, 151], petroleum ether [32, 129], carbon dioxide [14, 31, 148, 151], chloroform [151], and/or co-reactants, such as ethyl acetate [151], iso-propanol [150], acetic acid [14, 150], and water [14, 31, 130], have also been explored in systems involving RBL. For lipase-catalyzed (trans)esterification, the use of non-polar co-solvents like n- hexane is favorable as it avoids the removal of moisture or water from the lipase, keeping its active high, but may at certain proportions result in phase separation which may prevent the contact between the reactants and the catalyst itself [33]. Unlike co-solvents, whose roles are well established in improving miscibility and extraction of the lipids, the complexity of co-reactants' role and the reactions involved are not well investigated. However, from isolated systems involving different co-reactants, the improvements in yield may include the reactants serving as alkyl donors (acetates and alcohols), breakdown of solid matrix in the case of ISTE involving water and acetic acid [163–165], and/or the hydrolysis and acidolysis of acylglycerides to the more reactive FFA [137, 139, 142]. In most cases, the addition of co-solvents, and/or co-reactants, improves the productivity by reducing the reaction time required to achieve the same yield, or the reaction yield for a given reaction time. However, an effective use of co-solvent and co-reactants should not only be focused on the improvements in yields and shortening of reaction time but should also account for the overall solvent used and the relative ease of the subsequent separation steps as these would influence the overall productivity of the process. 3.5.3 Concentrations, solvent or alkyl donor loading, and catalyst loading In the synthesis and production of FAAE, system concentrations could be viewed in various perspectives, such as solvent or alkyl donor loading, in terms of solvent-to-lipid ratio (SLR), solvent-to-solid ratio (SSR), and catalyst loading, which is dependent on various other factors including catalyst activity, morphology, and textural properties of the catalyst. In most cases, these concentrations are expressed relative to one of the reaction components, typically, the amount of oils or lipids. Based on reaction stoichiometry, only 1 mole of alkyl donor is typically required for a mole of FFA and 3 moles for a mole of TG. To ensure that reactions are shifted forward, alkyl donors are often loaded in excess. In view of catalyst types used, enzyme-catalyzed systems typically require the least SLR and SSR (near stoichiometric requirements), followed by base-catalyzed, and then acid-catalyzed systems (Tables 3, 4, 5, and 6), while systems employing heterogeneous catalyst require higher SLR than those using a homogeneous catalyst (Table 3). Although higher SSR or SLR typically leads to better yields and conversions, the productivity of the reaction decreases for a given reactor volume and would require longer time and pose difficulties for later downstream processing. Moreover, excess SLR or SSR also results in a dilution effect, slowing down the overall reaction rate [16, 150]. From the perspective of reaction kinetics, assuming that the esterification and transesterification reactions involved are elementary reactions, these could be taken as a second-order reaction, but as one of the reactants is supplied in much greater excess, the reaction order may shift to a first-order reaction. Dilution does not only influence the reaction order but also the effective concentration of other components. Even if the ratio of certain components relative to the available lipid may be kept the same while another certain reaction component is varied, the overall concentration relative to the entire mixture is unavoidably changed. For instance, the increase in SLR or SSR at fixed catalyst loading relative to the available lipids inevitably dilutes the concentration of the catalyst concentra- tion in the overall mixture. The effective concentrations of the components involved significantly influence the overall reac- tion rate, and thus affect the productivity and pose difficulties in having a fair or objective comparison between reaction systems. In view of catalyst loading or concentration, higher catalyst loading is generally beneficial to the process but be- yond certain optimum, it may not be economical and may also cause problems in later downstream processing resulting in losses in the product as excess bases may result in saponifica- tion, while excess acid could result in unwanted hydrolysis of the BD produced. Perhaps not applicable for homogenous catalysts, excessive loading of heterogeneous catalysts may result in mass transfer limitation, thereby slowing down the reaction rate. As have been mentioned, most of the factors influencing the productivity of BD synthesis from RBL are interdependent and among them, temperature, solvent load- ing, and catalyst loading are the factors which closely affect one another having interaction effects, and are thus the factor mainly varied in the production of BD from RB. 3.5.4 Pressure, space loading, and reactor loading Unlike reactions involving gaseous reactant, operating pressure is in most cases not a factor for (trans)esterification or in the conversion of RBL to BD, except when a gaseous co-solvent like CO2 is used or when reactions are carried out under sub-/ supercritical conditions of at least one of the reactants. At a given temperature and system composition, the system pressure is indicative of the volume of the gaseous component in the system and the fraction of such components along with other components that are in the liquid phase. In the study by Yasmin et al. [152], increasing the system pressure to 10 MPa with CO2 resulted in improved yields of up to 98% as compared to sys- tems pressurized only at 4

12**MPa, which** had **a FAME yield of**

35%, after 3 h of reaction time at a reaction temperature of 200 °C with rice bran to methanol to water ratio of 1 g:4 cm3:4 cm3. Apart from the known improvement in solubility brought about by the presence of supercritical CO2, the improvement in FAME yield was also attributed to the more acidic reaction medium as CO2 is solubilized in water. Generally, higher pres- sures mean that more CO2 was being introduced into the sys- tem; therefore, for such complex systems involving various components, it would be critical to determine the actual quan- tity of carbon dioxide introduced to allow scale-up of the pro- cess. Furthermore, complexity and difficulties in estimating such quantity arise particularly when the available headspace of the reactor is not provided and whether the introduction of CO2 was done before the system was heated up or after the system was heated up. Aside from the introduction of gaseous components, the increase in system pressure may result from the expansion of the components involved in the reaction, particularly the alkyl donor and liquid co-solvents, and/or co-reactants added. For flow reactors, the pressure is regulated with pressure and back-pressure regulators along with changes in the system flow rates. However, for batch reactors, the available head- space and quantity of materials in the reactor influence the induced system pressure. In a review of ISTE by Go et al. [124], the influence of space and reactor loading was emphasized to be most relevant for (trans)esterification under sub-/ supercritical conditions. The concept of space loading was introduced by Lim and Lee [124] when intensifying the su- percritical ISTE of lipids in Jatropha curcas kernels, with the

2**space loading defined as the ratio of reactor volume to** that of **the** mass **of biomass loaded**

. In separate occasions, Go et al. [142, 143] introduced a similar concept but considered

2**the fraction of the reactor volume** initially **occupied by the reacting mixture**, referring **to**

it as the reactor loading, for either subcritical ISTE [143] or (trans)esterification of extract- ed lipids [142]. Both concepts are used to describe the effec- tive use of the reactor's volume, the available space for the reactants to expand, and indirectly indicate the amount of reactants in the vapor and liquid phases [124]. In the subcrit- ical ISTE of post-hydrolysis RB, Sutanto et al. [16] indicated that at a fixed SSR increasing the reactor loading improves the FAME yield but has tendencies to decrease beyond an opti- mum. An increase in reactor loading at a fixed SSR translates to more alkyl donor in the liquid phase which pushes the reaction forward, but could also result in dilution effects brought about by the excessive quantities of the alkyl donor or solvent as previously discussed. 3.5.5 Reactor type, mode of operation, and configuration Like most reactions, the (trans)esterification of RBL can be carried out using basic reactor types either stirred-tank or tu- bular reactors operated in batch or continuous mode. However, ISTE or OSETE are generally carried out in batch reactors, with these types of reactions carried out under sub- or supercritical conditions having the possibility of avoiding the need for stirring. Some notable reactor design, configuration, and operational mode that have been adopted in the (trans)esterification of RBL include packed-bed reactors [103, 110], and microreactors [150], operated in continuous mode. These continuous-flow reactors avoid the additional processing time for filling and discharging of materials into and out of the reactor and typically require smaller volumes. Packed-bed reactors for heterogeneous catalysts like immobilized enzymes [103] or ion-exchange resins [110] are characterized by the higher overall catalyst loading but may have the advantage of separating the catalyst from the reaction products, and the removal of by-products (glycerol and resid- ual free fatty acids) as these are adsorbed onto the catalyst matrix. As for microreactors, although not explicitly discussed, the required ethanol-to-oil of 5:1 [150] is lesser as compared to the required methanol-to-oil ratio of ~6 to 10 for typical tubular reactors [137]. For reactants having limited miscibility or inter solubility, the use of microreactors pro- vides the advantage of increasing the effective contact be- tween the two phases, reducing the required excess reactants. In general, the effective use of reactor configuration and op- erational modes in combination with certain RBL (trans)esterification process or synthesis routes may result in improved productivities by minimizing or avoiding the need for process start-up time, product separation and purification, and the possibility of minimizing the use of excess reactants and auxiliaries. 3.5.6 Kinetics and thermodynamics Kinetics and thermodynamic evaluations are means of evalu- ation to provide a more objective comparison between reacting systems. These are not factors affecting productivity but rather properties of a reacting system which may limit the achievable reaction yield. For reactions involved in BD syn- thesis, these are generally substitution reactions which are in principle reversible and have reaction orders (n) greater than 1. However, given that alkyl donors are often supplied in excess, the reactions are often assumed to be of the first-order and irreversible [120, 155]. Moreover, kinetics are often assessed at mixing conditions where mass transfer limitations are as- sumed to be negligible, allowing these reactions to be taken as pseudo-homogeneous reactions [156]. Although kinetic and thermodynamic parameters may take into account the influ- ences of different variables, it is not without limitations and is also limited to the assumption made when coming up with the model. In the transesterification of RRBO with methanol and eth- anol using a homogeneous catalyst (NaOH) under microwave irradiation [157], it was found that the activation energy (Ea) and frequency factor (A0) required for the reaction with etha- nol (Ea = 5.9 kJ·mol−1 A0 = 0.0388 s−1) are higher and lower, respectively, than that of methanol (Ea = 4.1 kJ·mol−1 A0 = 0.0251 s−1). These quantities provide quantitative support to the claim that methanol is more reactive than ethanol under the conditions (60 to 80 °C) investigated. However, kinetic exper- iments were carried out with fixed and higher alcohol to oil ratio for reactions with ethanol (9:1) than methanol (5:1) with catalyst loading at 0.15–0.18 wt% with respect to the RRBO. In a separate work dealing with a similar reaction but for a continuous reactor system, the ethanol to oil ratio employed was 5:1 with a catalyst loading of 0.6 wt%, the estimated kinetic parameters are as follows: Ea = 6.3 kJ·mol−1, and A0 = 0.7228 s−1 [160]. The higher frequency factor indicates the faster reaction rate that is achieved with higher catalyst loading. In a different study, employing heterogeneous catalyst (CaO) for transesterification of RRBO, Sreedhar and Kishan [155] estimated the kinetic parameters to be Ea = 25.7 kJ·mol−1, and A0 = 86.091 min−1 (1.4349 s−1),

3**at an** ethanol **to oil ratio of** 9:**1 and catalyst** loading **of**

3 wt.% over a

12**reaction temperature of 50** to 70 °**C**. Although the **reaction**

employed heterogeneous catalyst, the authors have proved that internal mass transfer could be neglected by determining the Thiele modulus to be less than 0.4, and thus, modeling the system to be a pseudo homogeneous first-order reaction. Because a dif- ferent catalyst was used, the reaction pathway is expected to be different and is indicated by the large difference in the determined activation energy. In view of esterification of FFA in high acid value RBL, there are also limited works which dealt with the reaction kinetics in detail. Esterification of RBL with acid value of 24 mg KOH·g−1 with H2SO4 as catalyst, a model assuming pseudo-homogeneous first-order forward reaction and second-order reverse reaction was adopted [19], with kinetic parameters of the forward reaction being Ea = 23.21 kJ·mol−1, and A0 = 32.65 min−1 (0.5442 s−1), and the reverse reaction having a higher activation energy 42.16 kJ·mol−1. Furthermore, the equilibrium reaction was assessed to be endothermic and non-spontaneous. Other high acid value RBL systems were investigated of their esterifica- tion kinetics employing heterogeneous catalyst, Fe2(SO4)3 [120], and 12-tungstophosphoric acid [123]. However, the kinetic parameters reported were not complete. Generally, detailed kinetic studies for the synthesis of RBL to BD have been limited. The absence of detailed kinetic pa- rameters may not be a hindrance to scaling up batch systems, but converting to other reactor configuration may be difficult. In the investigation and determination of kinetic parameters, a large difference in fatty acid composition also influenced the observed kinetic parameters [157]. This makes the direct com- parison of improved processes dealing with RBL with con- ventional or base-case processes employing other lipids not practical and using kinetic parameters from other lipids for reactor design not possible. Most kinetic models do not ac- count for the catalyst loaded and the amount of alcohol to lipid ratio. Moreover, some models have been oversimplified, which might have missed capturing the actual interactions of the reacting species and provide poor insights for the system being evaluated. In addition, modeling and determination of kinetic parameters have been limited to conventional homo- geneous, and heterogeneous processes, and only for either the esterification or transesterification. Kinetics of catalyst deacti- vation for heterogeneous catalysts are also of importance. Unfortunately, it has so far only been taken into account for Lipozyme® TL-IM catalyst in the (trans)esterification of high acid value RBL [103]. 3.6 Patented and emerging processing routes and technologies Apart from those published in academic journals, there are technological developments and advancements, which have been patented. A review of the patent landscape on the tech- nologies for biodiesel production has been published in 2020 by Mahlia et al. [166]. In this section, patents specifically for processing RBL to BD will be discussed along with technol- ogies or processes applicable for RBL but have not been ex- plored in actual converting RBL to DB. Moreover, novel ap- proaches in the maximized utilization of RB components as RBL is converted to DB are also looked into. 3.6.1 Patented technologies A recent review of the patented technologies for biodiesel production has indicated that there are about 1660 related patents from the period between January 1999 and July 2018 [166]. However, patents involving the conversion of RBL to DB are quite limited in comparison. In 2005, a patent involving the use of a base catalyst and relatively pure oils having moisture content of 0.5 wt% have been disclosed and could be adopted for use in the processing of RBO [166]. The said patent emphasizes carrying out the reaction at temperatures above the boiling point of the alcohol used but not exceeding 215 °C and under turbulent regimes of mixing (Reynolds Number > 4000). Furthermore, the said patent also emphasizes the purification and separation steps adopting bubble washing and microfiltration, respectively, with the entire process accomplished within a period of 50 h. A related patent for the processing of non-edible oils containing FFA has been disclosed in 2006, which involves a one-pot process but with 2 sequential steps, the first being acid-catalyzed esterification, and the second step is a base-catalyzed transesterification [167]. The emphasis of the patent is on the addition of a water scavenger or water adsorbent during the esterification step and with the excess base of the second step neutralizing the acid catalyst from the esterification step to have the entire synthesis carried out in one-pot. Since RBL or RBO has fatty acids very similar to other plant-based lipids or oils, the processes involved are often similar; however, there are also processes that have been uniquely developed for processing RBL to DB. ISTE via screw press and post-2-step acid-base (trans)esterification Although developed by Cantazani [168] for whole beans of castor oil plant, cottonseed, physic nut, or rice bran powder and perhaps applicable to other oil-containing materials, the use of a solvent assisted screw press extraction may be advantageous for processing RB considering its lipid content. The disclosed patent by Cantazani [168] involves the use of anhydrous ethanol as an extracting agent and the addition of sulfuric acid to facilitate ISTE even during the oil extraction step. Generally, RBL is extracted and simultaneously (trans)esterified using a screw press aided with an acidified anhydrous ethanol, and to ensure the lipids are completely converted, the extracted material is passed through a series of piston-cylinder reactors, which allowed acid-catalyzed esterification and base-catalyzed transesterification to further occur. As part of the claims in the said patent, the process can co-produce chemically enhanced organic fertilizers and that the process is feasibly designed for small-scale at 3 million gallons (~11,356 m3) of biodiesel per year. Sulfonic acid-functionalized quaternary ammonium salt as a reusable catalyst Another one-pot process patented for the processing of RBO containing FFA by Lin et al. [169] was filed and granted in China, where an ionic liquid (IL) is used as a catalyst. The said patent uses a quaternary ammonium salt functionalized with sulfonic acid as a catalyst for the (trans)esterification process, which has the advantage of being less corrosive and reusable. The said process is carried out at temperatures between 100 and 130 °C for 1–3 h with the molar ratio of RBO:Methanol:IL at 1:6–15:0.06–0.15. The described process could be adopted for RBO having an acid value of 1.5–107.36 mg KOH·g−1. Indigenous lipase in RB for ISTE Earlier works have made an emphasis on the observed hydrolytic activity of indigenous lipases found in RB [29, 30, 124], which causes the RBL to have high FFA during storage. The use of indigenous lipase in RB has been mentioned in a patent disclosed for the lipase-catalyzed conversion of beef tallow to BD in 2008 [170]. A unique and innovative means is implementing ISTE of RBL and taking advantage of the inherently available lipases. The patent was granted to Korean authors led by In-Hwan Kim in 2016 [171] and a related research article was published later in 2018 [172]. In the said technology, indigenous lipase in RB can be used to catalyze (trans)esterification by simply adding methanol to RB and allowing the reaction to proceed, or by utilizing the delipidated RB as a catalyst for the (trans)esterification of other oils, which could be reused up to 10 times. The ISTE process was found best at 40 °C with RB having a moisture content of 12 wt% and a methanol-to-lipid molar ratio of 6 over a reaction period of 12 days [172]. After a 12-day reaction cycle, only ~83% of FAME in the product is achieved, requiring the obtained products to be further (trans)esterified with dried spent RB for another 6 days at the same methanol loading and temperature as the first cycle to achieve complete conversion, with a product containing at least 95% FAME. Although the process is unique and may allow savings in terms of raw materials used, its productivity may be a bottleneck for actual industrialization. 3.6.2 Other alkyl donors and glycerol-free processes The synthesis or production of BD from RBL reported in the literature has so far only adopted the use of short-chain alco- hols as the alkyl donor and mainly reacted with the FA source to produce FAAE. There have been many strategies adopted in the production of BD or BD-like fuels over the years, which have been tested with plant-based lipids, widely used in the food industry like those from soybean, rapeseed, and sunflow- er, as well as in waste/used cooking oil, with the main goal of reducing or avoiding the generation of glycerol, while at the same time producing by-products of higher value or avoiding the need for purification after the reaction. Reviews on these synthesis routes have been written over the years, with the ones written by Calero et al. [173], Okoye and Hameed [174], and Esteves et al. [175] being the notable ones pub- lished in 2015, 2016, and 2019, respectively. Among the different alkyl donors introduced aside from alcohols are short-chain carboxylates and alkyl carbonates. Among the different carboxylates, methyl acetate is the most widely used for interesterification with the AGs to produce FAME and triacetin

14**in the presence of a** strong acid **catalyst** [176]. Compared **to glycerol**

as a by-product, triacetin need not require further separation and could be used along with the FAME as a biofuel. Such process has been patented and the fuel mixture named Gliperol® [176, 177]. In the presence of FFA, methyl acetate may undergo acidolysis and generate FAME with acetic acid as a by-product, which could easily be separated via distillation [134]. As for the use of alkyl car- bonates, dimethyl carbonate has been favorably explored, with by-products being fatty acid glycerol carbonates (FAGC), glyc- erol carbonate, and glycerol dicarbonate. The BD-like fuel mix- ture referred to as DMC-BioD® was patented with the process originally using sodium methoxide as catalyst and AGs as the main FA source [178, 179]. In the presence of FFA, glyoxal is produced as a by-product, which is said to be an industrially important precursor for many high-value derivatives [138]. Both methyl acetate and dimethyl carbonate were also success- fully used as alkyl donor in a catalyst-free process under super- critical conditions [134, 138, 180]. There are two main pur- poses in adopting these alkyl donors and these are to minimize the need to separate the by-products, or if by-products generat- ed are to be separated, these should be of better economic value than glycerol. In view of completely avoiding the generation of glycerol and the need to extensively purify the resulting reaction prod- ucts, other approaches have also been considered. To further ensure the greenness of the process, renewable reaction com- ponents, plant-based TGs, ethanol, and 1,3-regiospecific por- cine pancreatic lipase (PPL) are used during alcoholysis or par- tial transesterification, with the resulting products being

26**fatty acid ethyl** ester (FAEE) **and monoglycerides (MG**

). The pro- cess in producing such fuel mixture (Ecodiesel®) was original- ly developed and patented using either free or immobilized PPL [181, 182], but was later also produced via kinetically con- trolled base-catalyzed reactions [175]. Another perspective is the use of existing glycerol generated from existing BD indus- trial plants to produce MG and subsequently reacted with dimethoxymethane (DMM), to produce fatty acid formal glyc- erol esters (FAGE) and methanol, which could further react to produce FAME and glycerol formal (GF). The complex chain reactions occur in a one-pot process using an acid catalyst and are the latest addition to the patented process

26**which avoids the** generation **of glycerol as a by-product**

[183–186]. All these different BD-like fuel mixtures have been found to exhibit fuel properties similar to that of conventional BD and in most cases having better cold-flow properties while minimizing emissions when burned as fuel [134, 175, 182, 186]. Despite the developments and patents files as early as 2004, the use of these alkyl donors and approaches is not common in converting RBL to BD or BD-like fuel mixtures. 3.6.3

Maximized utilization of RBL lipids and components or bio-ref inery approaches The maximized use of biomass and its components as a feed- stock has long been practiced to maximize the greenness of the process and minimize the generation of waste. Earlier studies and reviews have focused on the recovery of bioactive components [17, 18, 94, 187] and proteins [188]. The follow- ing technologies that will be discussed will focus on those developed in recent years with the focus of primarily produc- ing biodiesel and at the same time maximize the utilization of other RB components, specifically carbohydrates/sugars, lik- ening a bio-refinery approach. One-pot synthesis of FAAE with reducing sugars/ethyl levulinate Treatment of biomass with water under subcritical condition was initially explored to release extractable and bound lipids from various biomass including activated sludge and yeast [165], sunflower and Datura stramonium seeds [164], and Jatropha curcas [144]. In the process of adopting such pretreatment, sugar-rich hydrolysates are generated and wet lipid-dense biomass could be subjected to ISTE with sol- vents under subcritical conditions and CO2 as co-solvent [144, 146]. A very similar approach was adopted by Zullaikah et al. [31, 130, 153] and Yasmin et al. [152] to carry out ISTE of RBL in the presence of subcritical water and methanol with CO2 as co-solvent to cogenerate hydrolysates containing re- ducing sugars.

1**At a** reaction **temperature of** 200 °**C**, an **SSR of 8** cm3·**g−1**

(methanol:water = 2–3 v:v), with the reaction sys- tem pressurized to 4–10 MPa with CO2, and allowed to react for 2 to 7 h, a FAME yield of 65–98% relative to the available lipids could be achieved along with sugars dissolved in the aqueous phase (0.6–0.8 g·L−1) [31, 153]. The lower sugar concentrations obtained at such conditions were attributed to the degradation of sugars to furans [31]. However, the rela- tively low concentrations are also influenced by the quantity of water added in the reaction and the latter washing step. Although high yields of BD could be achieved, the extent of the hydrolyzed sugars could not be assessed since the volume of hydrolysate or aqueous phase is not reported. The use of ethanol as the alkyl donor under similar condi- tions has also been explored, but intending to concurrently produce ethyl levulinate (EL) from the dehydration of avail- able sugars and subsequent esterification, as an additive for the BD produced [151]. The said process was reported to achieve FAME and EL yields of 78% and 10.9% relative to the maximum FAME, respectively, at 160 °C with 6.4 cm3 ethanol and 1.6 cm3 water per 1 g of RB and reacted for 2 h under CO2 atmosphere of 8 MPa. However, under such conditions, the purity of the product is only ~61 wt% in terms of FAME and ~8.5 wt% for EL, summing up < 70 wt% of biofuel. Although these approaches allow multiple products to be produced altogether, it may require a more complex pro- cess to further separate products before these could be used. Nevertheless, these approaches may be further developed while taking into consideration not only the extent of product generation but overall, the effective conversion of raw mate- rials to the desired product and the ease of their subsequent downstream processes.

1**Dilute acid hydrolysis** of RB **in the generation of**

raw materials for biofuels Apart from lipids, RB is rich in sugar, either in the form of starch, cellulose, or hemicellulose, which could con- stitute between 37 and 48 wt% of RB, depending on the RB fraction [33, 189]. The lipid content of most RB does not go beyond 20 wt%, which is considerably low when compared to oilseeds and oleaginous microorganisms [124]. On the ex- tremes, white RB (WRB), the innermost layer of RB, contains lipids as low as ~8 wt% but could be processed to obtain residues containing lipids over 20 wt% as have been reported in the study by Li et al. [33]. In the said study, WRB with lipid content of 8.43 wt% was subjected to enzymatic hydrolysis and yielded 0.45 kg glucose (~93% recovery) and 0.3 kg res- idue per kg of WRB processed. The said residue contained 29.31 wt% lipids, which is higher than typical RB and trans- lates to a lipid recovery or retention of ~104%. Although no details were provided, the recovery or retention of lipids over what was originally extractable may be attributed to the re- lease of structurally bound lipids. Adopting the same concept of removing structural components, while leaving behind the lipids via hydrolysis, Sutanto et al. [15, 16, 189] has also demonstrated the possibility of using dilute sulfuric acid (< 4 vol.%) solution as the hydrolyzing medium. Subjecting RB to dilute acid hydrolysis (DAH), most (~92%) of the structural sugars were converted into reducing sugars and yielding hy- drolysates containing reducing sugars at ~52 g·L−1 and 0.4 kg of residue per kg of RB processed [189]. The said residue was reported to contain 52.22 wt% lipids, which translates to a lipid recovery/retention of ~103%. This time around, Sutanto et al. [189] also provided a detailed investigation of the additional lipid released and suggested that these were indeed from structurally bound lipids. The DAH process typ- ically requires dilute acid containing 2 to 3 vol.% H2SO4,

9**SSR of 8** cm3·**g**−1 (**relative to the available lipid-free biomass**

), and subjected to hydrolysis at 95 °C for 3 to 6 h [15, 16, 189]. Through the hydrolysis of RB, not only is it possible to pro- duce hydrolysates rich in sugar but also residues that are lipid- dense (Fig. 5c). On different occasions, hydrolysates from DAH of non-delipidated RB was demonstrated to be useful as a substrate for fermentation and has been specifically used in the cultivation of Yarrowia lipolytica [189] and Lypomyces starkii [15] for lipid accumulation to also serve as feedstock for biodiesel production. Taking it a step further, Sutanto et al. [15, 16] have preliminarily investigated the use of the post-hydrolyzed rice bran (PHRB) as raw material for ISTE. The authors have observed that the residues were not only lipid-dense but also had catalytic activity as previously discussed (Section 3.4.3) and allows high FAME yields to be achieved in a relatively short reaction time and non-iso- thermally. To better understand the advantages brought about by the DAH of non-delipidated RB, Go et al. [190] have looked into the kinetics of

10**lipid extraction from** PHRB **with n-hexane as solvent. The**

authors were not only able to model the extraction kinetics but pro- vided insights on the possible ease and more rapid ex- traction of the lipids from PHRB than from the native RB with solvent savings of up to 80%. In certain cases, processes involving multiple steps offer the advantage of obtaining distinct products and avoid complex sepa- ration processes. Pretreatment processes like DAH may at first glance entail additional cost owing to the addi- tional steps introduced; however, it brings about value- added product(s) and eases the subsequent processing steps. 3.7 Foreseen impacts, challenges, and researchable gaps Economical impact Rice bran is an inevitable agro-industrial waste with a reliable availability and has been a source of continuous interest due to its potential applications, particular- ly in biodiesel production. Several technological advance- ments have prospered over the years exploring various mate- rials and process routes and conditions demonstrating BD production from RBL. Utilization of RBL as feedstock could possibly ease one of the hurdles limiting the use of BD, which is its economic feasibility. In a study by Haas et al. [191], they mentioned that 88% of the BD production cost is attributed to its raw material cost. This is also demonstrated by the Southeastern countries producing biodiesel from edible oil as reflected in the raw material to biodiesel cost ratio in Table 7. Atadashi et al. [192] mentioned that a potential of 25% can be reduced from the production cost by opting for a less premium feedstock. The utilization of RB could minimize or eliminate the gap between BD and PD cost, adding to the environmental motivation of BD consumption. With RB as a low-cost resource, this could mean that regions having access to such possibly could lower BD cost to support blending targets and improve the region’s buying power by generating high-value by-products from RBL. However, detailed opera- tions research on the collection and transport of RB from rice mills and technoeconomic analysis between different Biodiesel to Diesel Table 7 Cost of feedstock, biodiesel, and petroleum diesel based on available market data for 2018 from the respective country’s biofuel GAIN reports [28]. Raw Material to Petroleum Diesel Price Biodiesel Price Raw Material Price Feedstock Country Biodiesel Price Ratio Price Ratio US$/La Cots/L US$/La Cost/L US$/kga Cost 1.28 – 1.62 1.23 0.95 – 1.45 0.72 – 1.22 0.97 0.54 – 0.81 0.36 1.00 0.53 ± 0.04 7740±509 IDR/L 0.55 ± 0.04 5,150 IDR/L 0.69 ± 0.04 2.30±0.14 RM/L 0.56 ± 0.03 0.82 0.95 – 1.45 48.35 PHP/L 0.76 – 0.93 23 – 32 THB/L

0.76 – 1.06 0.70 – 85 0.57 ± 0.07 2.83±0.16 RM/L 46 – 70 PHP/L 23 – 28 THB/L 0.64 7482±634 IDR/kg 2.33±0.28 RM/kg 37.70±1.67 PHP/kg 0.78 ± 0.03 Crude Palm Oil Crude Palm Oil Philippines Coconut Oil Refined/Crude Palm Oil 19.57 THB/L Indonesia Malaysia Thailand a Conversion rates: 1 US$ = 14, 139 IDR = 4.12 RM = 48.18 PHP = 30.18 THB processes to produce BD from RB would have to be done to better grasp the practical extent of such potential resource. Social and environmental impact Other advantages of utilizing RBL production for BD are its lesser negative impact to the food versus fuel dilemma, and lower dependency on PD producing countries. Coincidentally and fortunately, regions with potential RB available for BD production are fervent users of BD with structured government mandates for blending except for China, Japan, and Bangladesh. Particularly, Wakil et al. [193] demonstrated the use of RB for BD production in their study and advocates it due to year-round cultivation which could optimistically significantly contribute to their diesel demand without competition in land use. In addition, Moreover, Subramaniam et al. [194] argues that usage of biofuels will also promote an increase in food production as an indirect result of better environmental quality in the long run. However, the actual use of biodiesel as fuel has been reported to have a pollutant profile with increased NOx and aldehydes compared to PD, but lower CO, CO2, and particulate matter [195]. Despite the number of different researches made related to diesel engine performance when using BD, there has been no consensus as to the most appropriate engineer operating configuration when adopting neat BD and its blends. Nevertheless, what is generally accepted is the fact that reduction in these emission could further be improved with proper configuration of engine operating conditions with blending of RB BD kept at 20 vol.% [24]. Government policies As with other novel undertakings which are aimed to be implemented and implanted, government programs and policies involving farmers and BD producers, customers and consumers must be in place. As a reference, the Brazilian government has a national program (PNPB) for biodiesel to ensure end-to-end stability of the entire biodiesel supply chain, from oilseed producers to biodiesel consumers through blending mandates [196, 197]. This program was designed to encourage small farmers to participate through ensuring oil sales by granting biodiesel producers fiscal benefits such as tax benefits, and favorable bank rates. This program also emphasizes diversification of feedstock sources and provides technical assistances to farmers. In the context of Asian nations, as the regions of interest for RB as feedstock to BD, blending mandates, and government support and subsidies are in place [198]; however, performance trending shows that they seem to fall short of their national targets [58]. Kumar et al. [199] stresses the need to expand biofuel feedstock from first generation to second generation for realization of blending targets, alongside necessary policy interventions. Amendments in the existing policies would have to include the establishment of support and infrastructures for rice farmers, on top of oilseed farmers, and take care of the tension that might occur due to the existing usage of RB such as livestock feed. Technical challenges and gaps The Asian regions and countries identified having the potential to utilize RB for BD production must first investigate the local quality ranges of their RB and its lipids, since the lipid content and quality largely depends on the PR variety and milling process undertaken. Technologically, the best choice for the production system to adopt depends on the local availability of materials, reactants and auxiliaries, and appropriate reaction systems apt to the desired production volume. However, a risk in process reliability is RBL's time-dependent deterioration of feedstock quality which will result to variable process requirements. This might also result to a risk in high production cost for a commodity, primarily considering flexibility. As demonstrated in the different researches discussed in previous sections, FFA content is a key factor in BD yields and process complexity, and its variability with time makes it more challenging. Because existing BD processes are conventional type employing homogeneous base as a catalyst and refined oils as feedstock, they could not be easily extended to the direct processing of RBL. As with typical lipid processing, solvent extraction might not be the most appealing first step, as demonstrated by the recently patented technologies, where ISTE systems have been chosen. This would also lift the requirement for large volumes of extracting solvent, and solvent recovery systems, agreeing to sustainability goals. A researchable area in this respect is the appropriate catalyst to be loaded to increase its challenge in low yields. Homogeneous catalysts, although the most convenient to use, also have an issue in wastewater generation. Immobilized enzymes are environmentally benign, require less alcohol, and milder operating conditions, but they have not yet been reported to be used in OSETE systems. Instead of choosing a catalyst, super or subcritical systems could be selected. In this respect, a lot of researchable areas arise including the kinetic, and equilibrium data, reactor load- ing, as well as process control to address the issue on low purity due to degradation. Another option for this system is the addition of co-reactants, such as acetic acid, as demonstrat- ed for subcritical system, however, knowledge on its actual role in the reaction is still not well understood. It should also be noted that the low purity in obtained product during ISTE may also be owing to the co-extraction of unsaponifiable com- ponents like oryzanol, which may serve as an antioxidizing agent in the final biodiesel product. Over the years, it has been demonstrated by various re- searchers that RBL could be transformed into biodiesel in several systems, starting with rice bran lipids subjected to conventional reaction system at ambient pressure, in situ system with rice bran biomass directly fed, and with these subjected to either supercritical and subcritical conditions of alcohols. Various reaction and process elements have been explored to improve yields and operational parameters such as reactants and catalysts and their concentrations, and reactor configurations. However, there has been no consen- sus as to how to best compare and report performance re- sponses, which would require detailed reporting of process conditions and further analysis based on quantitative met- rics. Finally, for complete valorization of RB, another valid process option is its maximum utilization into several prod- ucts. This can include isolation of its antioxidants for nutraceuticals, or co-production of bioethanol after employing DAH as pretreatment. As previously mentioned, these processes must be locally assessed at a reasonable scale for more conclusive process data useful in optimizing parameters and sustainability assessment. 4 Conclusions and recommendations One of the hurdles in the biodiesel industry is raw material cost, which could be addressed by utilizing oleaginous agro- industrial wastes. Rice bran has proven to be a valuable poten- tial feedstock owing to its high lipid content (15–25 wt%) and is widely available in Asia. Eastern, Southern, and Southestern Asia are found to have the largest production potential with about 2 million m3 annually for each region, which could con- tribute to at least 60% of the current biodiesel production in Asia. The use of RBL-derived BD could help reduce depen- dence on foreign fuel supply and use of petroleum diesel in Asia. Many RBL processing and subsequent synthesis routes to BD exist, each having their advantages and limitations, and has been reviewed in detail in this work. If RBL is to be ex- tracted first, solvent extraction is generally better than mechan- ical extraction in terms of recovery. The use of enzymes or biomass-based catalyst and/or with sub- and supercritical sol- vent reaction technologies are promising greener processing routes and alternatives to conventional acid and base- catalyzed processes. In the direct processing of RBL in RB, ISTE with appropriate pre-processing like dilute acid hydroly- sis (DAH) is a good core step in an integrated process for RB- BD and co-product synthesis. Like another chemical reactions, conversion of RBL to BD is greatly influenced by the process temperature, concentration of reacting components (reactants, catalysts, and co-solvents), quality of mixing as induced me- chanical action, irradiation and/or improving reactant inter-mis- cibility, and reactor type, configurations and operation, which at the same time are to some extent interdependent and are influ- enced by one another. Variabilities in RB and RBL composi- tion require detailed kinetic and equilibrium data must be col- lected at an appropriate scale and reaction scheme to better design a robust reaction process system. To move forward with the utilization of RB for BD, it would be necessary to have preliminary characterization RB for a given locality to better understand its quality and the technology to be adopted, follow- ed by a conduct of a techno-economic and environmental eval- uation of the promising technologies at a valid scale for a more conclusive assessment. In parallel, strategies and possible infra- structures required in the efficient collection and transport of RB generated in each locality should be carefully studied. Countries should also reevaluate their biodiesel mandates, roadmaps, and their action plans on propagation of diversified feedstocks to bridge towards targets and incorporate the use of RB as a resource or feedstock. Acknowledgements

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