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REVIEW

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Conversion of residues and by-products from the biodiesel industry into value-added products

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Abstract

Biodiesel, one of the most important sources of renewable energy, is produced in large quantities around the world; however, its production generates different kinds of residues and by-products which raise economic and environmental concerns. This review presents a compilation of the data on current state of transformation of residues and by-products of biodiesel industry into products that are suitable for bio-refining. The review has analyzed glycerol, biodiesel washing wastewaters, and solid residues. The technologies were described and the most significant experimental results and variables were summarized to allow researchers an easy access to this information.

Keywords: Biodiesel, Waste glycerol, Biodiesel washing wastewaters, Fermentation, Thermal conversion

Background

The extensive use of fossil fuels has generated environmental issues, such as global warming and atmospheric pollution (Siles et al. 2010). The replacement of fossil fuels for renewable biofuels is a necessity. The employment of biofuels from biological feedstocks is a significant option because they can be generated sustainably from sunlight, carbon dioxide, and water (Juang et al. 2011). Biodiesel is one of the most prominent biofuels in the world. Biodiesel is the name given to the fatty alkyl esters produced after transesterification of fatty acids using methanol or ethanol in the presence of a catalyst such as sodium hydroxide. To produce biodiesel, oils from different sources can be used. They are obtained from plants oil (palm, soy bean, sunflower, etc.) or animal fats (chicken, beef, and pork). Because biodiesel can be produced using different types of plant or animal oil, its production can be developed in most places around the world. The traditional technology is fully developed and technologically accessible. For example, in 2010, 19 billion L of biodiesel were produced worldwide (Global Renewable Fuels Alliance 2012) and its production has been increasing constantly over the last few years (Rossi et al. 2011).

The production of biodiesel in large quantities also results in the generation of abundant quantities of residues or by-products which cannot be utilized in biodiesel production process (Eliche-Quesada et al. 2012). Therefore, new applications to treat and use these compounds have become an important topic. In biodiesel, the most significant residues and by-products are glycerol, biodiesel washing wastewaters, methanol, and solid residues (Varanda et al. 2011). Glycerol is the by-product that generates the largest interest, because it can involve the largest revenue for the biodiesel industry. Glycerol is the main by-product from biodiesel transesterification (Nitayavardhana and Khanal 2011; Ethier et al. 2011); by 2016, the worldwide waste glycerol production is expected to reach 4 billion gallons (Yang et al. 2012). However, the glycerol produced from biodiesel has low quality and low price ($0.05 per pound) and its purification for further applications is economically unviable (Nitayavardhana and Khanal 2011). The largest residue produced by the biodiesel industry is the biodiesel washing wastewaters from the biodiesel washing process. The projected production of biodiesel for 2016 is 37 billion gallons, this amount of biodiesel will produce 43 billion

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gallons of wastewaters (Yang et al. 2012; Siles et al. 2011). This large amount of residues is related with disposal and environmental issues, because these wastewaters have a high organic load that does not allow its direct disposal into the sewage system (Rattanapan et al. 2011). Solid by-products are the residues that include pressed seed cakes, spent earth, and agricultural wastes. The biological solid residues are generally used in compost or for animal feeding; however, these compounds can increase the profitability of the biodiesel industry if they can be utilized as a substrate for the production of chemical compounds or energy.

The aim of this review was to summarize the current state of art in the transformation of the most significant biodiesel by-products and residues.

Biodiesel by-products and residues

Glycerol

1,2,3 propanetriol or commonly named as glycerol, glycerin, or glycerine is an organic compound with three carbons and three hydroxyl groups. Glycerol is mainly produced by saponification process and is widely utilized in pharmaceutical and food industry (Ethier et al. 2011). Besides the saponification process, glycerol is an abundant by-product of biodiesel production process. Crude glycerol is the name given to the glycerol produced during biodiesel production (Dobroth et al. 2011; Ethier et al. 2011) and is a by-product of transesterification reaction that takes place between the fatty acids with methanol or ethanol to produce methyl esters. Crude glycerol represents about 10 % of the product output in biodiesel production (Sousa et al. 2012); in fact, 1 kg of crude glycerol is produced per 12.6 L of biodiesel (Dobroth et al. 2011). Crude glycerol is considered as a residue because residual ethanol or methanol, fatty acid ethyl (or methyl) esters, and residual fatty acids are mixed with it (Dobroth et al. 2011). These impurities can be removed from crude glycerol to produce a raw material for pharmaceutical and food industries. The crude glycerol purification and refining is very expensive to be sustainable in the biodiesel industry (Ethier et al. 2011; Sabourin-Provost and Hallenbeck 2009). Therefore, the utilization of crude glycerol is important for the biodiesel industry future. The application of crude glycerol can be grouped into bioproduct's production (Rossi et al. 2012; André et al. 2010; Abad and Turon 2012), renewable energy production (Yoon et al. 2010; Ngo et al. 2011), and wastewater applications (Siles López et al. 2009; Bodík et al. 2009).

Bioproducts

The transformation of glycerol into bioproducts is performed by physicochemical or microbial processes. Physicochemical process transforms glycerol, or it utilizes glycerol as a participant in the production of other bioproducts. Hydrothermal electrolysis transforms glycerol into lactic acid using aqueous alkaline conditions at high temperatures and pressures (Yuksel et al. 2011). In this case, a designed autoclave and a flow type reactor were evaluated. The autoclave achieved a glycerol conversion of 83 %, whereas the flow type reactor accomplished a 75 % (Yuksel et al. 2011). Other waste glycerol uses are the production of castor oil glycerides and polyols. Glycerolysis of castor oil methyl esters and waste glycerol generated castor oil monoglycerides (50.4 %) and diglycerides (35 %) which can be employed in the plastic industries (Echeverri et al. 2013). On the other hand, polyols were produced from a sequential two-step liquefaction of lignocellulosic material using crude glycerol as liquefaction solvent. In this process, acid and base liquefactions promoted the esterification reaction between free fatty acids and glycerol and the condensation of polyols. These biopolyols had similar properties as those of the petroleum-based polyols (Hu and Li 2014).

Microbial transformation has been carried out for the production of oxalic and docosahexaenoic acid (Ethier et al. 2011), polymer-related molecules [polyhydroxybutyrate (PHB) and 1,3-propanediol] (Dobroth et al. 2011), surfactants (Sousa et al. 2012), and animal feed (Nitayavardhana and Khanal 2011). Table 1 shows the microbial transformation methods. To increase the concentration of bioproducts from crude glycerol, different strategies have been used. The most significant ones are genetic engineering, media and environmental condition's optimization. Genetic engineering has been employed to improve synthesis of different types of products. These improvements include genes insertion that allows consumption of crude glycerol and/or the production of different types of molecules. *Escherichia coli* was genetically modified by inserting the aldehyde reductase and aldehyde dehydrogenase genes, these genes improved the generation of poly 3-hydroxybutyrate (Shah et al. 2014). *Corynebacterium glutamicum* was genetically modified to increase the concentration of different types of amino acids (Meiswinkel et al. 2013). Likewise, free fatty acid concentration was improved by using an *E. coli* with a modified OPLlTE gen. This modification increased free fatty acids by 15.8 fold compared to the control (Lee et al. 2014). Recombinant engineering is an interesting option to improve the production of biobased products from waste glycerol. The cost of manipulating and maintaining these microorganisms needs to be considered. This technology improves the up-stream process; however, the principal cost in biotechnological processes is related with the recovery and purification costs. The developments in genetic engineering should be focused in improving the recovery and purification of these

Table 1 Bioproducts produced by microbiological transformation of crude glycerol

Product	Microorganism	Initial glycerol	Yield	References
Biosurfactants	*Bacillus* sp.	2 % (v/v)	–	(Sousa et al. 2012)
Polyhydroxybutyrate	Mixed microbial consortia	10 % (v/v)	–	(Dobroth et al. 2011)
1,3-Propanediol	*Klebsiella pneumoniae*	10 % (v/v)	0.41 mol/mol	(Rossi et al. 2012)
Docosahexaenoic acid	*Schizochytrium limacinum*	90 g/L	1.74 g/L	(Ethier et al. 2011)
Ethanol	*Enterobacter aerogenes*	80 mM	0.96 mol/mol	(Ito et al. 2005)
Oxalic acid	*Aspergillus niger* NRRL *Aspergillus niger* LFMB	60 g/L 60 g/L	0.55 g/g 0.61 g/g	(André et al. 2010)
Animal feed	*Rhizopus microsporus*	75 %	0.83 g/g	(Nitayavardhana and Khanal 2011)
Docosahexaenoic acid	*Schizochytrium limacinum*	75–100 g/L	4.91 g/L	(Chi et al. 2007)
1,3-Propanediol	*P. agglomerans, C. freundii*	60 g/L 20 g/L	0.56 g/g 0.68 g/g	(Casali et al. 2012)
Poly 3-hydroxybutyrate bioethanol	*Escherichia coli*	30 g/L	0.8 g 30.2 %	(Shah et al. 2014)
1,3-Propanodiol (1,3-PD)	*C. butyricum*	80 g/L	2.75 g/L/h	(Szymanowska-Powałowska and Leja 2014)
Lipids	*Chlorella protothecoides*	30.55 wt%	2.07 g/L/h	(Feng et al. 2014)
Polyhydroxyalkanoates	Mixed microbial cultures	30 mg/L	0.27 g/L/d	(Moita et al. 2014)
p-Hydroxybenzoate	*Pseudomonas putida* S12	18.4 g/L	6.0 g/L	(Verhoef et al. 2014)
L-Glutamate L-Lysine L-Ornithine L-Arginine Putrescine	*Corynebacterium glutamicum*	20 g/L	0.026 g/g 0.08 g/g 0.12 g/g 0.03 g/g 0.03 g/g	(Meiswinkel et al. 2013)
Dihydroxyacetone	*Gluconobacter frateurii*	15 g/L	125.8 g/L	(Liu et al. 2013b)
Free fatty acids	*Escherichia coli*	10 g/L	231 mg/g	(Lee et al. 2014)
1,3-Propanediol	*Lactobacillus diolivorans*	10 g/L	0.36 g/L/h	(Pflügl et al. 2014)
Biomass	*Yarrowia lipolytica*	25 g/L	12.3 g/L	(Juszczyk et al. 2013)
1,3-Propanediol	Mixed microbial consortia	7 g/L	0.65 mol/mol g	(Liu et al. 2013a)
1,3-Propanediol	*Citrobacter freundii*	176 g/L	66.3 g/L	(Metsoviti et al. 2013)
Fumaric acid	*Rhizopus arrhizus*	80 g/L	4.37 g/L	(Zhou et al. 2014)
n-Butanol	*Clostridium pasteurianum*	10 g/L	0.35 g/g	(Khanna et al. 2013)
Organic acids Trehalose	*Propionibacterium freudenreichii*	20 g/L	0.42 g/g 0.90 mg/g	(Ruhal and Choudhury 2012)
Lipids	*Rhodotorula glutinis*	30 g/L	5.40 g/L	(Yen et al. 2012)

bioproducts. The most important modification to the culture media was nitrogen concentration. The change in nitrogen concentration increased the quantity of 1,3-propanediols and docosahexaenoic acid (Sabourin-Provost and Hallenbeck 2009; Chi et al. 2007). Bioproduct's microbial processes have been evaluated using different types of reactors configurations. Packed bed reactor was employed in the production of 1,3-propanediol (Casali et al. 2012), whereas stirred tank reactors have been operated for docosahexaenoic acid (Ethier et al. 2011) 1,3 propanediol (Rossi et al. 2012) and polyhydroxyalkanoates (PHA) (Dobroth et al. 2011). Fed-batch configuration produced dihydroxyacetone in quantities (2–5 fold) greater than batch culture (Liu et al. 2013b). Microfiltration was coupled to a batch reactor to improve the production of 1,3-propanodiol by *C. butyricum*. This modification achieved a larger yield and rate than the batch reactor without microfiltration (Szymanowska-Powałowska and Leja 2014).

In the last few years, the microbiological transformation of crude glycerol has become an interesting option to utilize crude glycerol and to increase the efficiency of biodiesel production process. Today, an industrial process using crude glycerol does not exist; however, several products have been generated from glycerol using biological transformations. As an example, an estimate of 19 tonnes per year of bioplastics (PHB) can be produced from a biodiesel plant of 38 million L per year (Dobroth et al. 2011). The potential for bioproduct from waste glycerol is great; however, the industrial recovery of these bioproducts is a major issue. Downstream processing is expensive, especially for products that are in low concentrations. In those cases, the bioproducts need to have a high value, therefore, the capital and production costs can be recuperated by the process. The future industrialization of bioproducts from glycerol is dependent of the economic aspects related with the advances in product recovery. Until these developments are not available, the industrial production of biobased product from waste glycerol is distant.

Renewable energy production

Renewable energy can be produced from crude glycerol using thermochemical or biological processes. The principal thermochemical processes include pyrolysis and gasification, whereas the most important biological processes are biological fuel cells, hydrogen generation, and anaerobic digestion (biomethane production).

Thermal conversion Thermal conversions (gasification and pyrolysis) and biomass fuel cells are the two physicochemical processes used to generate energy from crude glycerol. Gasification and pyrolysis are performed at high temperatures (>300 °C) in an atmosphere which lacks oxygen or has a small quantity of it. These processes generate a gas phase (synthesis gas or Syngas), liquid phase (bio-oil or bio-liquor), and a solid phase (biochar). Each phase percentage is dependent of the reaction conditions. In these processes, the most important conditions are temperature, pressure, residence time, air to O_2 ratio, and catalyst. Table 2 shows the thermal processes used in the transformation of crude glycerol into biofuels.

Pyrolysis studies have been performed using crude glycerol as an auxiliary compound to pyrolyze different types of feedstocks. The mixture of crude glycerol and swine manure improved the quality of bio-oil and its distillated fractions compared with the pyrolysis of swine manure alone (Cheng et al. 2014a). The addition of glycerol has been found as a factor to improve hydrogen (H_2) concentration in the Syngas. The addition of 20 % of glycerol to lignite generated H_2 sixfold higher than lignite pyrolysis (Manara and Zabaniotou 2013). Similar to lignite, olive kernel pyrolysis exhibited an increment of 11.6 % in the concentration of H_2 when 25 % of the crude glycerol was added (Skoulou et al. 2012). Besides the increment in H_2 concentration, glycerol also increased the concentration of light hydrocarbons in Syngas. A mixture 1:1 or 3:1 of crude glycerol and corn straw produced a twofold increment in C4 and C5 hydrocarbons compared with corn straw pyrolysis (Delgado et al. 2013).

Crude glycerol gasification used traditional processes; however, microwave plasma gasification and Supercritical Water Gasification have also been employed to gasify crude glycerol. Traditional crude glycerol gasification is performed in a co-gasification process. Crude glycerol has been gasified along with olive kernel, hardwood chips, physic nut waste, and palm shell waste (Sricharoenchaikul and Atong 2012; Wei et al. 2011; Rattanapan et al. 2011; Skoulou and Zabaniotou 2013). The co-gasification of crude glycerol and biomass incremented Syngas yield, heating value, and H_2 concentration (Sricharoenchaikul and Atong 2012; Wei et al. 2011; Rattanapan et al. 2011; Skoulou and Zabaniotou 2013). The Syngas produced from the crude glycerol co-gasification can be further employed to generate electricity or to produce chemicals or biofuels (Skoulou and Zabaniotou 2013). On the other hand, microwave plasma gasification is a technology that utilizes plasma flames produced by external electrical sources to gasify substrates. Crude glycerol microwave plasma gasification demonstrated an increment in gasification efficiency and Syngas heating value (Yoon et al. 2013). Another type of gasification is supercritical water gasification. This technology utilizes supercritical water to improve the gasification efficiency. Supercritical water has the ability to act as an acid/base catalyst, dissolve non-polar organic compounds, and react with other compounds (Tapah et al. 2014). The application of supercritical water gasification in crude glycerol has been evaluated in the presence of KOH and $Fe_2O_3–Cr_2O_3$ as catalysts (Yang et al. 2013; Tapah et al. 2014). Catalytic supercritical water gasification improved the Syngas quality by reducing biochar impurities and increasing the amount of combustible gases, especially H_2. However, KOH did not act as a catalyst; in fact, KOH acted as a reactant in the process and generated K_2CO_3 as the product (Yang et al. 2013).

Thermal conversion is an option for the transformation of glycerol into energy and other chemicals. In this type of process, crude glycerol is an interesting option as a co-substrate for gasification or pyrolysis processes. Therefore, the combination of a thermal conversion plant and biodiesel production can be an option for the biodiesel industry. The thermal conversion plant can use the agricultural residues (stems, leafs, stalks, husk, etc.) and the pressed seeds as main substrate, whereas waste glycerol can be employed as a co-substrate to increase the quality of the Syngas or the bio-oil produced. In this case, the viability will depend on the economic and logistic analyses for the thermal conversion plant.

Microbial fuel cells Microbial fuel cell is other approximation to physicochemical energy generation. This process employs microbial strains to catalyze the oxidation of organic or inorganic matter for electricity generation (Feng et al. 2011). Feng et al. (2011) found that it is possible to produce electricity using crude glycerol as substrate for microbial fuel cells. In their research, a maximum cathode power density of 2110 mW/m^2 was obtained from the

Table 2 Crude glycerol thermal conversion

Process	Co-substrate	Glycerol concentration	Conditions	Products	References
Batch pyrolysis	Swine manure	1:3 swine manure:crude glycerol	340 °C for 15 min	Bio-oil	(Cheng et al. 2014b)
Co-gasification	Olive kernel	49 wt%	750–850 °C Air ratio: 0.2–0.4	Syngas (10.5–52.2) Bio-oil (2.4–19.5) Biochar (37.9–78.3)	(Skoulou and Zabaniotou 2013)
Co-gasification	Hardwood chips	20 (wt%)	850 °C Air ratio: 0.293	CO (19.73 % v) CH_4 (3.82 % v) H_2 (19.38 % v) CO_2 (11.67 % v)	(Wei et al. 2011)
Pyrolysis	Greek lignite	15–20 wt%	850 °C	H_2 (65.44 v/v %)	(Manara and Zabaniotou 2013)
Slow co-pyrolysis	Corn straw	1:1 glycerol:corn straw	30 °C/min, 550 °C	Syngas (25 %) Bio-oil (55 %) Biochar (15 %)	(Delgado et al. 2013)
Co-gasification	Physic nut waste (pnw) Palm shell waste (psw)	30 %	700–900 °C Air ratio: 0–0.6	pnw Syngas (95.41 wt%) psw Syngas (94.70 wt%)	(Sricharoenchaikul and Atong 2012)
Pyrolysis	Olive kernel	25 wt%	720 °C	H_2 (45 %)	(Skoulou et al. 2012)
Microwave plasma gasification	–	100 %	Air ratio: 0–0.4 2 kW microwave generator	H_2 (57 %) CO (35 %)	(Yoon et al. 2013)
Catalytic supercritical water gasification	–	30 wt% glycerol	600 °C at 300 bar	H_2, CO, CO_2, CH_4	(Tapah et al. 2014)
Supercritical water gasification	–	7 wt%	500 °C, 45 MPa	H_2 (27.9 %)	(Yang et al. 2013)
Gasification	–	60 %	950–1500 °C	H_2 (38–42 %) CO (39–41 %) CO_2 (9–15 %) CH_4 (1–3 %)	(Yoon et al. 2010)

heat-treated anode of the microbial fuel cell with biodiesel waste medium (Feng et al. 2011).

Hydrogen generation Hydrogen is the most studied biofuel from crude glycerol. Hydrogen is produced by dark fermentation and photofermentation processes (Rossi et al. 2011; Ghosh et al. 2012b). Table 3 describes the different processes used in hydrogen production from crude glycerol.

Dark fermentation employs anaerobic or facultative microorganisms in a process similar to anaerobic digestion. This fermentation has been improved by modifying the microorganisms, the culture media, or the reactor conditions. The bacteria applied normally came from methanogenic fermentation including several types of hydrogenic bacteria (Rossi et al. 2011); however, the strains have been improved using molecular techniques (transgenic strains) (Gonzalez et al. 2008) or selection techniques (eco-biotechnological) (Varrone et al. 2013b), and these methodologies have allowed the increment of H_2 generation and glycerol consumption. In dark fermentation, culture medium has achieved improvements in the hydrogen production. Rossi et al. (2011) found that biomass pretreatment before glycerol conversion improved the hydrogen yield by fivefold. This process reduced the methanogenic bacteria in the sludge which was added as the inoculum (Rossi et al. 2011). Ngo et al. (2011) improved the hydrogen yield (1.55–2 fold) compared with the un-supplemented culture by using a buffer solution (N-2-hydroxyethylpiperazine-N′-2-ethanesulfonic acid) and N_2 sparging conditions (Ngo et al. 2011). Similarly, Sarma et al. (2013a) found that slaughterhouse liquid waste, brewery waste biomass, and urea increased the H_2 generation by *Enterobacter aerogenes NRRL B 407* from 18 to 38 % (Sarma et al. 2013a). The addition of KH_2PO_4 and NH_4Cl maximized the hydrogen (0.27 mol/mol) and ethanol (0.63 mol/mol) yields from crude glycerol using *Klebsiella* sp. TR17 (Chookaew et al. 2014b). The modification of the growth media can be introduced by reducing the inhibitor concentrations. Methanol and

Table 3 Hydrogen production from crude glycerol

Product	Microorganism	Initial glycerol	Yield	References
Photofermentation	*Rhodopseudomonas palustris*	20 mM	6.1 mol/mol	(Ghosh et al. 2012b)
Dark fermentation	*Klebsiella pneumoniae*	10 % (v/v)	31.16 mol/g	(Rossi et al. 2011)
Photofermentation	*Rhodopseudomonas palustris*	10 mM	4.0 g/g	(Sabourin-Provost and Hallenbeck 2009)
Dark fermentation	*Clostridium pasteurianum*	10 g/L	0.775 mol/mol	(Lo et al. 2013)
Dark fermentation	*Klebsiella* sp. TR17	10 g/L	44.27 mmol/g	(Chookaew et al. 2014a)
Photofermentation	*Rhodopseudomonas palustris*	30 mM	7 mol/mol	(Ghosh et al. 2012a)
Dark fermentation	*Enterobacter aerogenes* NRRL B-407	10 g/L	2.51 mmol/L	(Sarma et al. 2013b)
Dark fermentation	Microbial mixed culture	90 %	0.66 mol/mol	(Varrone et al. 2013b)
Dark fermentation	*Enterobacter aerogenes*	20 g/L	25 mmol/L	(Sarma et al. 2014)
Photofermentation	*Rhodopseudomonas palustris*	10 mM	34 ml/g/h	(Pott et al. 2013)
Dark fermentation	*Enterobacter aerogenes* NRRL B 407	10 g/L	116.41 mmol/L	(Sarma et al. 2013a)
Dark fermentation	*Klebsiella* sp. TR17	11.14 g/L	0.27 mol/mol	(Chookaew et al. 2014b)
Photofermentation	*Rhodopseudomonas palustris*	50 mM	23–27 ml/g/h	(Pott et al. 2014)
Dark fermentation	Microbial mixed culture	20 g/L	9 L/L	(Varrone et al. 2013a)
Dark fermentation	Microbial mixed culture	50 %	0.55 mol/mol	(Chookaew et al. 2014a)

saponified-free fatty acids (SFFA) were found as inhibitors of hydrogen production by *Enterobacter aerogenes* NRRL B 407 (Sarma et al. 2013b). The SFFA was also found as the most important inhibitor. The removal of this inhibitor was evaluated using salting out and $MgCl_2$ reactions. Salting out removed 42 % of SFFA; however, it also decreased the carbon/nitrogen ratio, producing an inhibition of the H_2 production. On contrary, addition of $MgCl_2$ transformed SFFA into its inactive form (scum), increased H_2 cumulative production (34.70 %), and glycerol utilization (2.5-fold) (Sarma et al. 2014). The reactor type and configuration have been evaluated to increase the H_2 production from glycerol. The employment of a continuous reactor in the culture of *Clostridium pasteurianum* augmented the production of H_2 compared to the batch reactor (Lo et al. 2013). The immobilization of *Klebsiella* sp. *TR17* in an upflow anaerobic sludge blanket (UASB) reactors increased the H_2 yield and hydraulic retention time (Chookaew et al. 2014a).

Photofermentation is the bio-hydrogen production from organic matter in the presence of light. Photofermentation is normally performed using organic acids; however, some purple non-sulfur photosynthetic bacteria can also transform glycerol into bio-hydrogen directly (Ghosh et al. 2012a; Sabourin-Provost and Hallenbeck 2009). *Rhodopseudomonas palustris,* a purple non-sulfur photosynthetic bacterium, incremented the hydrogen yield 6 times compared with *Enterobacter aerogenes* or *E. coli* (Ghosh et al. 2012b). *Rhodopseudomonas palustris* increased hydrogen production in cultures with high nitrogen concentration (Sabourin-Provost and Hallenbeck 2009) and by optimizing crude glycerol concentration (30 mM), glutamate concentration (4.5 mM), and light intensity (175 W/m^2) (Ghosh et al. 2012a). Similar to dark fermentation, photofermentation is highly inhibited by SFFA. Pott et al. (2013) demonstrated that SFFA is the most important inhibitor in crude glycerol, generating a reduction in the growth rate of *R. palustris* (Pott et al. 2013). To reduce the SFFA concentration in the crude glycerol, Pott et al. (2014) evaluated different techniques (ethanol and activated carbon, pH adjustment, solvent extraction, and precipitation of the fatty acids with calcium) to reduce SFFA concentration. The best two treatments included pH adjustment and SFFA precipitation with calcium salts. These two treatments (23–27 ml/g/h) generated similar hydrogen yields as highly purified glycerol (29 ml/g/h) (Pott et al. 2014). Besides the large hydrogen yields, photofermentation also needs to improve light use by *R. palustris* and this raises the need to develop economic hydrogen permeable photobioreactors (Ghosh et al. 2012a; Sabourin-Provost and Hallenbeck 2009).

Anaerobic digestion In anaerobic digestion, crude glycerol is employed as the principal carbon source (Hutňan et al. 2013) or as a complementary carbon source (Siles López et al. 2009) to improve denitrification processes (Bodík et al. 2009) or methane generation (Álvarez et al. 2010). Table 4 shows the details of the crude glycerol anaerobic digestion. Hutňan et al. (2013) evaluated the efficiency of using crude glycerol in an UASB reactor. They improve the methane yield by diluting previously acidified crude glycerol, these modifications generated high chemical oxygen demand (COD) removal, and methane production (Hutňan et al. 2013). In the work of Siles López et al. 2009, the stoichiometry reaction for crude

Table 4 Crude glycerol anaerobic digestion

Co-substrate	Glycerol concentration (%)	pH/temperature/ °C	Retention time (days)	Methane yield	References
Sewage sludge	1 (v/v)	5/35	33	2353 mL/day	(Fountoulakis et al. 2010)
Sewage sludge	3	7/37	12.3	0.8 L/g TVS	(Athanasoulia et al. 2014)
Sewage sludge	0.63 (v/v)	7/35.0	20	1.3 m^3/L crude glycerol	(Nghiem et al. 2014)
Wastewaters	47	6.88/35.0	30	2.17 g/L/day	(Watanabe et al. 2013)
–	80	7.6–8.9/37	1	0.9 L/mL	(Hutňan et al. 2013)
Orange peel waste		7.19/35	8.5–30.0	330 mL/g VS	(Martín et al. 2013)
Pig manure	3	55	15	0.47 L/g^{-1} VS	(Astals et al. 2013)
Pig manure and fish waste	8	7.0–7.2/35	15.6	16.4 L/kg COD/day	(Álvarez et al. 2010)

VS volatile solids, *TVS* total volatile solids, *COD* chemical oxygen demand

glycerol was found: $C_3H_8O_3 + aNH_3 \rightarrow bCH_4 + cCO_2 + dC_5H_7NO_2 + eNH_4HCO_3$, where the values of a, b, c, d, and e were 0.663, 1.648, 0.526, 0.041, and 0.622 mol, respectively (Siles López et al. 2009). The evaluation of anaerobic treatment of crude glycerol was made using pretreated glycerol (distilled and acidified) and granular or non-granular sludge. In this, work the highest methane yield was obtained by granular sludge-distilled glycerol; even so, granular sludge and acidified glycerol achieved the highest glycerol degradation (100 %) and an appreciable methane yield (Siles López et al. 2009).

Crude glycerol has been used principally as a co-substrate for different types of compounds such as sewage sludge, manure, and food wastes. Large concentration of crude glycerol has been inhibitory in the anaerobic digestion of sewage sludge; in fact, the recommended concentration is around 0.6–3 %. However, the crude glycerol addition increased the methane yield around 2–4 times compared with the control (Fountoulakis et al. 2010; Athanasoulia et al. 2014; Nghiem et al. 2014). Similar to sewage sludge, pig manure anaerobic digestion was improved by the addition of crude glycerol. Alvarez et al. (2010) found that methane generation can be maximized by anaerobic co-digestion of crude glycerol with pig manure and fish wastes. The highest methane production rate (16.4 L CH_4/kg COD/day) was reached mixing 89 % of pig manure, 4 % of fish wastes, and 8 % of crude glycerin (Álvarez et al. 2010). Likewise, Astals et al. 2013 incremented the methane generation in 180 % by adding 3 % crude glycerol (Astals et al. 2013). Crude glycerol has been identified as a sustainable carbon source for denitrification processes. In the work of Bodik et al. (2009), the addition of crude glycerol into a denitrification process increased almost 2.5 fold the denitrification efficiency with a reduction of 5 ppm NO_3/100 L of crude glycerol (Bodík et al. 2009). Crude glycerol anaerobic digestion manages large volumes, produces energy, and has a low price (Bodík et al. 2009). However, anaerobic digestion did not produce products with higher value.

Anaerobic digestion is an option to utilize waste glycerol and produce energy. Similar to thermal conversion, glycerol is not used as a main substrate; however, it can be sold or supplied to other anaerobic digestion plants or the biodiesel plant that can include anaerobic digestion reactors to treat the organic wastes produced from the biodiesel production. Anaerobic digestion is a more developed and less expensive technique than thermal conversion.

Biodiesel washing wastewaters

After the transesterification reaction, the methyl esters are separated from glycerol and the biodiesel is subjected to purification process to remove impurities (Suehara et al. 2005). The principal impurities are the remaining oil and methanol, residual catalyst, soap, and glycerin (Phukingngam et al. 2011). Impurities removal consumes approximately 20 L of water to 100 L of biodiesel (Suehara et al. 2005); this process is repeated 2–5 times depending on the amount of impurities present in the methyl esters (Phukingngam et al. 2011). At the end, the washing process generates between 20–120 L of wastewater from 100 L of biodiesel produced (Rattanapan et al. 2011). Biodiesel washing wastewaters (BWW) are alkaline ($pH \approx 9$), have high chemical oxygen demand (COD) (60,000–545,000 mg/L), and grease and oil (G&O) (7000–44,300 mg/L) (Rattanapan et al. 2011). However, these wastewaters will have low nitrogen and phosphorus compounds, which make their biological treatment a challenging topic (Suehara et al. 2005; Rattanapan et al. 2011; Phukingngam et al. 2011). Biodiesel washing wastewaters need to be treated before being released into the environment because, without any such treatment, the existing compounds can produce drainage plugging, and decrease biological activity of the sewage treatment plants (Suehara et al. 2005). The general treatment methodology utilized over this residue starts with an initial pretreatment for G&O reduction followed by a treatment for COD reduction. However, in recent years, the application of adsorption technologies has modified the BWW treatment. Table 5 summarizes the treatment and pretreatment technologies used for washing wastewaters.

BWW pretreatment avoids COD degradation inhibition (Phukingngam et al. 2011). The pretreatment technologies are chemical or physicochemical. The chemical pretreatment utilizes strong acids to remove G&O (Ngamlerdpokin et al. 2011). In this pretreatment, the protons from the acid produce a coalescence effect over the oil drops making them to move until they reach upper part of the solution (Rattanapan et al. 2011). Additionally, protons can neutralize residual alkali catalyst in biodiesel wastewater and substitute the Na atom in soap molecules formed in the transesterification reaction (Ngamlerdpokin et al. 2011). Strong acids such as H_2S0_4, HCl, and HNO_3 have been employed in these pretreatments; however, the best results were obtained by H_2S0_4 with a pH of 2 or lower (Rattanapan et al. 2011; Ngamlerdpokin et al. 2011). The most used physicochemical pretreatment is electrocoagulation. In this pretreatment, the wastewater is placed in a reactor which produces an electric field that generates flocculating agents (aluminum related) capable of removing the G&O or COD particles (Chavalparit and Ongwandee 2009).

After pretreatment, BWW have been treated using anaerobic digestion or coagulation agents. Coagulation is a physicochemical treatment that reduces G&O or COD concentrations in the BWW. The principal types are electrochemical and chemical coagulation (Ngamlerdpokin et al. 2011). Chemical coagulation utilizes an external coagulant agent to bond different particles of G&O or COD in small groups, which can be easily removed by the addition of a flocculating agent (Ngamlerdpokin et al. 2011). On the contrary, electrochemical coagulation utilizes an electrical field to generate its own coagulant agent. In both coagulations, the most common flocculating agents produced or introduced are aluminum related. Aluminum compounds are recognized by its best properties in coagulation and flocculation processes (Siles et al. 2011). The most important factors in electrocoagulation are voltage, pH, and reaction time. In chemical coagulation, the important factors are concentration, pH, and reaction time (Ngamlerdpokin et al. 2011; Rattanapan et al. 2011). Coagulations have showed efficient removal of G&O when they are utilized as pretreatment or treatment agents. However, coagulation only could achieve substantial COD removal when it is performed after a previous pretreatment (Chavalparit and Ongwandee 2009; Jaruwat et al. 2010).

Biodiesel washing wastewater anaerobic treatment is another option besides coagulation. Similar to coagulation, anaerobic digestion needs to pretreat BWW to reduce G&O and COD (Bezerra et al. 2011). Pretreatment processes allowed efficient COD and G&O reduction using anaerobic treatment; nevertheless, high concentrations of some chemicals from the pretreatment can be harmful for the anaerobic process (Siles et al. 2011). In addition to COD and G&O removal, anaerobic process produces considerable amount of methane, with removals around 278–305 mL CH_4/g COD removed, which is about 88 % of the possible methane yield from COD (Siles et al. 2011; Bezerra et al. 2011).

Table 5 Treatments applied to wastewater from biodiesel washing process

Pretreatment	Treatment	Initial COD (g/L)	COD removal (%)	Initial G&O (g/L)	G&O removal (%)	References
Dilution	Anaerobic process	14.8	100	15.1	98	(Suehara et al. 2005)
Acidification	Anaerobic process	56.4	99	3.3	84	(Phukingngam et al. 2011)
Acidification and electrocoagulation	Dissolved air flotation	150	90	15	90	(Rattanapan et al. 2011)
	Electrocoagulation	30	55	6	97	(Chavalparit and Ongwandee 2009)
Acid protonation	Chemical coagulation	312	99.6	4.2	97	(Ngamlerdpokin et al. 2011)
Acid protonation	Electrocoagulation	312	97.5	4.2	98.2	(Ngamlerdpokin et al. 2011)
Acidification, electrocoagulation	Anaerobic process	300	100	–	–	(Siles et al. 2010)
Acid protonation	Electrochemical coagulation	588	100	22	100	(Jaruwat et al. 2010)
	Electrospun polystyrene membrane	445	75	–	–	(Shirazi et al. 2013)
Acidification	Chitosan flakes adsorption	0.015, 0.71–0.73, 0.12	90	0.68–1.19	67	(Pitakpoolsil and Hunsom 2013)
Acidification	Chitosan flakes adsorption	0.021, 0.24–31, 0.3	97.6	0.680–1.130	95.8	(Pitakpoolsil and Hunsom 2014)

In the last few years, BWW has been treated using adsorption and membrane technology to reduce the COD and G&O concentrations. Shirazi et al. 2013 evaluated electrospun microporous membranes before and after surface modification to reduce the COD from BWW. The modified membrane achieved the largest reduction in COD (75 %). This technology did not use any type of pretreatment to reduce COD or G&O concentration, which is an advantage over the other BWW treatments (Shirazi et al. 2013). Similar to membranes, chitosan adsorption is another alternative for treating BWW. Chitosan flakes considerably reduce the concentrations of COD (90 %) and G&O (67 %), at 3.5 g/L chitosan, pH 4, and 3 h of incubation (Pitakpoolsil and Hunsom 2013). To improve this treatment, four successive treatments were tested. This modification enhanced BOD, COD, and G&O removal up to 93.6, 97.6, and 95.8 %, respectively (Pitakpoolsil and Hunsom 2014).

Anaerobic process and coagulation have similitudes in the degradation level; both processes achieved values up to 85 %. The duration of the process is variable; anaerobic treatment is a slow process which takes 30–40 days (Bezerra et al. 2011); however, coagulation takes only 20 min to 1 h (Ngamlerdpokin et al. 2011). Anaerobic process and membrane technologies have a reduced cost compared with coagulation; the first ones do not have any additional price and anaerobic digestion has the advantage of producing energy from methane which could be sold or utilized in the biodiesel plant. On the other hand, coagulation processes need the presence of coagulants and large quantities of energy to run the reactors; these factors eventually increase the process costs.

Treatment of other biodiesel residues

Besides glycerin and BWW, biodiesel production produces other residues. These are produced in lower quantities or have characteristics allowing the utilization of conventional treatment techniques. Methanol is one of these residues, and it can be easily recovered using distillation techniques. Methanol recovery systems such as flash distillation (Wang et al. 2011) or vacuum distillation (Varanda et al. 2011) are available in the market. These techniques remove the methanol efficiently without affecting the transesterification process because of the differences between the boiling points in their components (Varanda et al. 2011).

Pressed seed cakes, spent earth, and agricultural wastes from biodiesel crops are also residues from the biodiesel production. Pressed seed cakes are the seed biomass leftover from oil extraction. This solid residue is normally used as an organic amendment, animal feed, or is composted (Varanda et al. 2011). Recently, seed cakes have been evaluated for hydrogen generation. Lopes et al. 2015 used dark fermentation to produce hydrogen from pretreated and untreated jatropha seed cake. The highest specific bio-hydrogen yield (68.2 mL H_2/g VS) was achieved using 2.5 g VS of untreated jatropha seed cake; however, the largest cumulative concentration was achieved with 10 g VS (Lopes et al. 2015). Likewise, Panagiotopoulos et al. (2013) evaluated dark fermentation of cotton-seed cake. *Caldicellulosiruptor saccharolyticus* produced significantly higher hydrogen yield (84–112 %) than the control. However, hydrogen was only generated when the cotton-seed cake was pretreated with NaOH (10 %) (Panagiotopoulos et al. 2013). In a different approach, seed cakes have been used in solid-state fermentation to produce edible fungus and enzymes (Veerabhadrappa et al. 2014; da Luz et al. 2013). da Luz et al. (2013) described the production of the edible fungus *Pleurotus ostreatus* from jatropha seed cake; this fungal strain degraded the antinutritional factors in the jatropha seed cake (da Luz et al. 2013). Similarly, Veerabhadrappa et al. (2014) reported proteases and lipases from *Aspergillus versicolor* CJS-98 in the solid-state fermentation of jatropha seed cake. The fermentation of jatropha seed cake with medium supplementation (maltose and peptone 2 %), 40 % moisture, and 25 °C produced maximum amount of proteases (3366 U/g) and lipases (1288 U/g) and removed jatropha seed cake anti-nutrients (Veerabhadrappa et al. 2014). Pressed seed cakes and agricultural wastes from biodiesel crops have also been studied for activated carbon production (Foo and Hameed 2009; Nunes et al. 2009). Activated carbons from biofuel solid residues are produced via thermochemical conversion, in a two-step process: first, the removal of residual oil and second, the thermochemical activation using temperatures between 600 and 800 °C under constant N_2 flow (Nunes et al. 2009). From the biofuel agricultural residues, it is possible to produce low-cost activated carbons with wide superficial area and good uptake capacity; however, more research is needed to develop an activated carbon which can be applied in water purification or wastewater treatments (Foo and Hameed 2009).

Bentonites soaked in biodiesel also called spent earth are a residue produced from biodiesel polishing process. In this step, saturated bentonites with a biodiesel concentration of 20–50 % are obtained. The oil in the bentonites can be treated by chemical extraction; similar to biodiesel production from vegetable oil. Besides that, this residue has been evaluated to produce environmentally friendly, low-cost, and lightweight construction materials. In the work of Eliche-Quesada et al. (2012), glycerin and spent earth were mixed with clay to produce lightweight bricks (Eliche-Quesada et al. 2012). The addition of oil containing bentonites (at 15 %) into the clay generated ceramic insulation bricks with reduced thermal conductivity and reduced energy costs (Eliche-Quesada et al. 2012).

Summary

Biodiesel is one of the most important sources of renewable energy; however, biodiesel production is associated with by-products and residues generation. Numerous techniques have been developed to utilize or to treat biodiesel by-products or residues. These techniques have shown that the above residues can be used to generate bioproducts and renewable energy. These processes and techniques can also reduce environmental pollution and increase the opportunities to generate additional income or reduce the costs of production of biodiesel. Invention of advanced technologies to deal with these residues could also make the biodiesel production process more sustainable and competitive against fossil fuels.

Abbreviations

BWW: biodiesel washing wastewaters; COD: chemical oxygen demand; G&O: grease and oil; PHA: polyhydroxyalkanoates; PHB: polyhydroxybutyrate; SFFA: saponified-free fatty acids; TVS: total volatile solids; UASB: upflow anaerobic sludge blanket; VS: volatile solids.

Authors' contributions

JP was responsible of manuscript drafting and writing. SC was responsible of final manuscript approval. Both authors read and approved the final manuscript.

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Competing interests

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