Recent trends in biodiesel production

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HIGHLIGHTS

- Recent trends and innovations in biodiesel production were comprehensively reviewed.
- Upstream, mainstream, and downstream strategies for economizing biodiesel production were elaborated.
- Integrated strategies for enhancing sustainability of biodiesel production processes were discussed.

GRAPHICAL ABSTRACT

ABSTRACT

This article fully discusses the recent trends in the production of one of the most attractive types of biofuels, i.e., biodiesel, with a focus on the existing obstacles for its large scale production. Moreover, recent innovations/improvements under three categories of upstream, mainstream, and downstream processes are also presented. Upstream strategies are mainly focused on seeking more sustainable oil feedstocks and/or enhancing the quality of waste-oriented ones. The mainstream strategies section highlights the numerous attempts made to enhance agitation efficiency including chemical and/or mechanical strategies. Finally, the innovative downstream strategies basically dealing with 1) separation of biodiesel and glycerin, 2) purification of biodiesel and glycerin, and 3) improving the characteristics of the produced fuel, are comprehensively reviewed.

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Biodiesel is attracting an increasing deal of attention worldwide for it is currently the only renewable energy carrier which could directly replace diesel fuel in compression ignition engines. Moreover, life cycle analysis (LCA) data for biodiesel suggests positive cumulative energy values when compared to petroleum-derived diesel (Vonortas and Papayannakos, 2014). Besides, biodiesel chemically known as monoalkyl esters of long chain fatty acids (FAME) (Singh and Taggar, 2014), also sustains many other advantageous features. Those include reduction of most exhaust emissions in comparison with petrodiesel, higher cetane number, biodegradability, lack of sulphur, inherent lubricity, positive energy balance, higher flash point, compatibility with the existing fuel distribution infrastructure, renewability, and domestic origin (Hajari et al., 2014). The last feature not only could potentially secure a continuous, consistent, and economic feedstock supply, but also could provide opportunities for indigenous development of especially rural and isolated regions (Pinzi et al., 2014).

Among the many challenges yet to be overcome before one could portray biodiesel as a sustainable alternative for decades to come is an economic feedstock supply. In fact, it is now well-documented that the price of feedstock could account for 70-88% of the total biodiesel production cost and hence is considered as the most significant factor affecting the economic viability of the biodiesel market (Hasheminejad et al., 2011). The most common feedstocks currently used in biodiesel production are vegetable oils derived from edible oil crops, such as rapeseed, palm, soybean, and sunflower. However, biodiesel from edible oils is controversial to the extent that even in a number of occasions high food market prices and diminishing supply.

Alternative Fuel Price Report (2015), released by the United States Department of Energy (US-DOE) (US-EIA, 2014), argued that based on their preliminary financial analysis, the economic viability of the whole biodiesel production process is doomed to change dramatically over time if edible oil crops are no longer an option. Thus, to provide non-competitive biodiesel (with food) in a sustainable and reasonably-priced manner, utilization of non-edible oil crops would be beneficial.

2. Strategies for economizing biodiesel production

Therefore, given the fact that the main interest is increasingly shifting towards larger scale biodiesel production, and also due to the above-mentioned existing obstacles, there is a strong market drive for more innovative, integrated, and efficient processes. Such innovations/improvements fall under three categories of upstream, mainstream, and downstream processes while integration of these processes is of great interest for it could enhance the economic viability of the whole biodiesel production process.

2.1. Upstream strategies

Such solutions mainly deal with seeking more sustainable oil feedstocks and/or enhancing the quality of waste-oriented ones.

2.1.1. Waste-oriented oil feedstocks

Apart from WFO, which has been a focus of numerous studies, other waste oil resources of no commercial value such as spent bleaching earth (SBE) oil (Sahafi et al., 2015) and soapstocks (Azocar et al., 2010) have also been proposed. It also should be noted that animal fats/lipids such as chicken fat, tallow, lard, waste fish oil (Sharma et al., 2014) and so on are not truly of no commercial value for they are in high demand in many parts of the globe as food/feed ingredients and hence, are not considered as ideal waste oil feedstocks for sustainable biodiesel production practices.

Annual global production of WFO is estimated at around 17 million tonnes (Gui et al., 2008) which if all collected, could have well supplied 50% of the total oil demand for the approximately 30 million tons of biodiesel produced in the year 2014. However, despite the growing efforts in increasing the WFO share in the market, this valuable waste oil feedstock is still under-utilized. For instance, in the United States, only less than 20% of the 4.5 million tons biodiesel generated in the year 2014 was of WFO origin (US-EIA, 2014).

SBE is an industrial waste generated in the vegetable oil refining industry after bleaching process of the crude oil (Canackci and Gerpen, 2003) and could contain 20 - 40 %wt. oil. SBE may present a fire hazard if not properly stored or disposed of at landfills (Sahafi et al., 2015). Huang and Chang (2010) estimated that on average 0.5 million tons of SBE oil is generated annually in the world. Sahafi et al. (2015) argued that based on their preliminary financial analysis, the economic feasibility and availability of SBE residual oil would make it a better option for biodiesel production than using the refined vegetable oil or WFO. Moreover, a number of studies reported significant improvements in the properties and performance of biodiesel-diesel fuel blends by dissolving waste polymers such as expanded polystyrene (EPS) in biodiesel produced from WFO and SBE oil (Mohammadi et al., 2012, 2013, 2014). Such a strategy not only offers an innovative way of...
recovering energy contained in waste polymers but also, given the achieved improvements reported, could enhance the economic features of waste-oriented biodiesel.

Soapstock is a by-product from vegetable oil refinement (Pinzi et al., 2014). In 2009, the worldwide generation of soybean soapstock alone stood at 2.16 million tons, 6% of the soybean oil produced in the same year (Azocar et al., 2010). Despite of its considerable global production quantity, when compared to WFO and SBE oil, soapstock does not stand a chance in terms of quality. This is ascribed to soapstock’s high water content of about 50% wt. which is also difficult to be removed because it is emulsified with lipids (Pinzi et al., 2014). Waste oil recovered from edible oil mills effluents through the application of novel technologies such as electrosynap fibrous filters (Sundaramurthy et al., 2014) can also be considered as a low-cost, widely available, emerging, and interesting source for biodiesel production (Shirazi et al., 2014a).

The main disadvantageous features shared by all these waste oil resources are their high FFA content (which can reach values up to 12%) and low oxidative stability. The Former has to be dealt with prior to the reaction as it negatively affects the common alkaline transesterification process through saponification reaction reducing the biodiesel yield, preventing the separation of biodiesel-glycerin phases, and finally increasing the washwater generated (El Sabagh et al., 2011). A number of methods have been proposed so far in order to pre-treat WFO to ensure FFA content of below 0.5% wt. (Zhang et al., 2003). These include steam injection (Lertsathapornsuk et al., 2005), column chromatography (Kh-Teak and Foglia, 2002), ion-exchange resins (Shibasaki-Kitakawa et al., 2007), neutralization by film vacuum evaporation (Cvengros and Cvengrosova, 2004), vacuum filtration (Dias et al., 2008), and finally the most usual procedure of esterification of FFA with homogeneous or heterogeneous acid catalysts (Table 1) (Ghadge and Raheman, 2005; Chung et al., 2008; Zhang and Jiang, 2008; Lu et al., 2009; Bojan and Durairaj, 2010; Hayyan et al., 2010; Montefrio et al., 2010; Kombe et al., 2012; Ouachab and Tsoutsos, 2012).

2.1.2. Non-edible oil crops

Non-edible oil crops such as Jatropha curcas, Calophyllum inophyllum, Nicotiana tabacum, Ceiba Pentandra, Calophyllum inophyllum, and Hevea brasiliensis are considered highly sustainable feedstocks for biodiesel production provided that they result in no competition over water or land used for conventional agricultural practices. In better words, these crops should be cultivated on marginal lands where no irrigation is performed. Laying such hard conditions would make it difficult for non-edible oil crops to catch up with the currently profitable biodiesel market mostly (>80%) relying on edible oil crops. Moreover, non-edible oil feedstocks are also known for their high FFA content requiring pretreatment (Sivakumar et al., 2013).

On the other hand, it is worth mentioning that the properties of biodiesel produced from oil feedstocks including non-edible oil crops strongly depend on fatty acid profile of the oil (Talebi et al., 2013). Talebi et al. (2014) recently introduced the BiodieselAnalyzer software capable of predicting properties of a prospective biodiesel solely based on the fatty acid methyl ester (FAME) profile of the oil feedstock used. The bioprospecting software could cover a wide range of biodiesel quality parameters, i.e., unsaturation level (including saturated and unsaturated fatty acids, degree of unsaturation), cetane number, cold flow properties (including cloud point and cold filter plugging point), oxidation stability (including allylic and bis-allylic position equivalents and oxidation stability), higher heating value, kinematic viscosity, and density. This could lead to an insight into the quality of the produced product and would eliminate the need for lengthy and costly production and analysis steps. The software is available on the public domain at http://www.brteam.ir/biodieselanalyzer.

Silitonga et al. (2013) compared the quality parameters of biodiesel produced from a number of certain oil feedstocks used in their investigation and the values reported for the same crops in the literature. They confirmed significant variations in some parameters resulting from different fatty acid profiles of the oils used (Table 2) (Ramadas et al., 2005; Sarin et al., 2007; Sulistyo et al., 2008; Devan and Mahalakshmi, 2009; Ong et al., 2011; Mozifir et al., 2012; Silitonga et al., 2013).

2.1.3. Unicellular oil feedstocks

Microalgae is a feedstock that may help meet the growing global demands for biodiesel while posing potentially fewer environmental/food security threats than conventional oil feedstocks of either edible or non-edible nature. This is ascribed to the fact that not only these autotrophic

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<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Catalyst conc. (% wt. oil)</th>
<th>Methanol: Oil molar ratio</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Initial FFA amount (mg KOH/g)</th>
<th>Post-treatment FFA amount (mg KOH/g)</th>
<th>Conversion (%)</th>
<th>Operating cost (USD/ton oil)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric acid</td>
<td>2%</td>
<td>24:1</td>
<td>60</td>
<td>0.5 min</td>
<td>45.51</td>
<td>1.2</td>
<td>97</td>
<td>718</td>
<td>Zhang and Jiang, 2008</td>
</tr>
<tr>
<td></td>
<td>20%</td>
<td>35:1</td>
<td>40</td>
<td>1 h</td>
<td>53</td>
<td>1.2</td>
<td>97</td>
<td>1152</td>
<td>Ouachab and Tsoutsos, 2012</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>12:1</td>
<td>60</td>
<td>0.5 h</td>
<td>38</td>
<td>4.8</td>
<td>87</td>
<td>366</td>
<td>Ghadge and Raheman, 2005</td>
</tr>
<tr>
<td></td>
<td>1%</td>
<td>9:1</td>
<td>60</td>
<td>1 h</td>
<td>13.7</td>
<td>2.3</td>
<td>83</td>
<td>272</td>
<td>Bojan and Durairaj, 2010</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>16:1</td>
<td>60</td>
<td>2 h</td>
<td>11</td>
<td>0.6</td>
<td>95</td>
<td>484</td>
<td>Kombe et al., 2012</td>
</tr>
<tr>
<td>Mordenite</td>
<td>1%</td>
<td>30:1</td>
<td>60</td>
<td>3 h</td>
<td>1.25</td>
<td>0.2</td>
<td>80.9</td>
<td>935</td>
<td>Chung et al., 2006</td>
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<tr>
<td>Metatitanic acid</td>
<td>4%</td>
<td>20:1</td>
<td>90</td>
<td>2 h</td>
<td>14</td>
<td>0.4</td>
<td>97</td>
<td>1190</td>
<td>Lu et al., 2009</td>
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<tr>
<td>PTA</td>
<td>0.75%</td>
<td>10:1</td>
<td>60</td>
<td>4 h</td>
<td>43</td>
<td>3.9</td>
<td>90</td>
<td>305</td>
<td>Hayyan et al., 2010</td>
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<tr>
<td>Solid acid</td>
<td>0.2%</td>
<td>16:8:1</td>
<td>220</td>
<td>4.5 h</td>
<td>NA</td>
<td>NA</td>
<td>80.5</td>
<td>525</td>
<td>Montefrio et al., 2010</td>
</tr>
</tbody>
</table>

* Post-treatment FFA amount (mg KOH/g) of ≤1 has been reported as suitable for proceeding with alkali-catalyzed transesterification reaction (Montefrio et al., 2010).

* In order to calculate the overall cost of each procedure, the following assumptions were made:
  - For economic assessment, average prices were considered as follows: industrial methanol at 800 USD/ton; industrial grade sulfuric acid at 600 USD/ton; PTA (95%-98% resin catalyst) at 1400 USD/ton; carbonized vegetable oil asphalt at 12000 USD/ton (100 ml sulfuric acid is required for production of 5 g carbonized vegetable oil asphalt); metatitanic acid at 15000 USD/ton; mordenite molecular sieve at 5000 USD/ton.
  - All calculations were made for pretreating 1 ton oil feedstock and the cost of equipment was not taken into consideration.

* NA: not available.
microorganisms can be cultivated and harvested continuously throughout the year (Chen et al., 2011), but some also grow extremely fast doubling their biomass within a day (Chisti, 2008). Moreover, despite sharing the same basic photosynthetic machinery as the C3 land plants (Chisti, 2013a), microalgal species are more efficient in converting sunlight to biochemical energy; 5-8% vs. 2.4-4.6%, respectively (Zhu et al., 2008; Stephenson et al., 2011; Chisti, 2013b). Such high theoretical productivities and oil accumulation concentrations from 0.02–0.5% (Brennan and Owende, 2010; Lundquist et al., 2010). Therefore, for algal biodiesel to be economically attractive, these bottlenecks should be removed. Membrane-based processes have come to the center of attention in various applications including algal biomass processes during the last decade due to their several advantages, e.g., high efficiency under mild operational conditions, compact equipment, low operational time/energy, ease of integration with other processes, and high process scale-up capacity (Shirazi et al., 2013a; Bilad et al., 2014; Shirazi et al., 2014b, c; Shirazi and Tabatabaei, 2014; Shirazi et al., 2015). However, membranes also suffer from several drawbacks restricting their large-scale application in algal fuel production. These include concentration polarization, membrane fouling, low membrane life-span, low selectivity, and permeance (Bilad et al., 2014). Mostly commercially-available organic polymer-based membranes, due to their wide availability, high chemical compatibility, variety of designs and reasonable cost (Strathmann, 2011), have been investigated for microalgae harvesting so far (Gerardo et al., 2014).

In a recent attempt, Shumran et al. (2014) successfully tested an ultra-low energy method for rapid pre-concentrating microalgae using electro-coagulation-flocculation method. They managed to achieve rapid separation of >90% of microalgal cells within 120 min while >90% of the cells were still alive after processing. The minimum energy density input required for effective separation in their study was 0.03 kWh/m². This was significantly lower that the required energy input (ranging from 0.3 to 2.23 kWh/m² (Bhave et al., 2012; Buckwalter et al., 2013; Gerardo et al., 2015)) for the membrane-based separation processes reported in the literature.

Finally, two methods of algal oil transformation could be performed 1) a two-step method, i.e., oil extraction followed by oil transesterification and 2) single step in situ transesterification of algal oils to biodiesel (Daroch et al., 2013). Having said all, algal biodiesel is not destined to reach its economically viable commercialization stage till the cost of producing algal biomass is reduced significantly. In an estimate, Chisti (2013a) argued that algal biomass with an oil content of 40% wt. has to be produced at a cost of ≤$0.25/kg, if algal oil is to compete with petroleum given its current price of $100/barrel. He concluded that the actual cost of producing the biomass at present appears is at least 10-fold greater. Chisti (2013a) also insisted that widespread use of algal fuels is unlikely in the short run but specific applications such as in aviation may be likely in the medium term. Finally, genetic and metabolic engineering of microalgae to enhance oil production and to ease its recovery seem indispensable parts of algal biodiesel commercialization scenario in the long run (Tabatabaei et al., 2011; Chisti, 2013a; Talebi et al., 2014).

Cyanobacteria, oxygenic photosynthetic bacteria, play a significant role in global biological carbon sequestration, oxygen production and the nitrogen cycle (Parmar et al., 2011). Similar to microalgae, cyanobacteria demonstrations plants (ABO, 2015), which have generated less than 500 tons of algal biodiesel during the years 2013 and 2014 (US-EIA, 2014). As a result, most existing large-scale microalgal plants are currently aimed at producing high-value products such as nutrition supplement and cosmetics instead of biofuels since for such compounds using energy-intensive centrifugation-based harvesting system is economical (Brennan and Owende, 2010; Lundquist et al., 2010). Therefore, for algal biodiesel to be economically attractive, these bottlenecks should be removed. Membrane-based processes have come to the center of attention in various applications including algal biomass processes during the last decade due to their several advantages, e.g., high efficiency under mild operational conditions, compact equipment, low operational time/energy, ease of integration with other processes, and high process scale-up capacity (Shirazi et al., 2013a; Bilad et al., 2014; Shirazi et al., 2014b, c; Shirazi and Tabatabaei, 2014; Shirazi et al., 2015). However, membranes also suffer from several drawbacks restricting their large-scale application in algal fuel production. These include concentration polarization, membrane fouling, low membrane life-span, low selectivity, and permeance (Bilad et al., 2014). Mostly commercially-available organic polymer-based membranes, due to their wide availability, high chemical compatibility, variety of designs and reasonable cost (Strathmann, 2011), have been investigated for microalgae harvesting so far (Gerardo et al., 2014).

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as oil-producing unicellular organisms also offer unique features including fast cell growth, simple nutrient requirements, i.e., water, sunlight, and CO2 (Ruffing, 2011). Equally important, they are naturally transformable and as a result could be potentially improved by genetic engineering (Machado and Atsumi, 2012). Due to their natural diversity, the capacity of cyanobacteria to grow in a variety of locations, even those unfit for agriculture, could be exploited for biofuel production. Karatay and Dönmez (2011) investigated a number of thermophile cyanobacteria for biodiesel production. They reported lipid contents of 42.8% for Synechococcus sp., 45.0% for CyanoBacterium aponinum, and 38.2% for Phormidium sp. under optimum conditions. Liu et al. (2010a) genetically engineered the cyanobacterium Synechococcus elongates PCC7942 in order to increase FFCA content and achieved a production efficiency of up to 133 ± 12 mg/L per day at a cell density of 0.23 g of dry weight per liter. This was almost 3 folds higher than the lipid content achieved in a genetically engineered E. coli strain (Liu et al., 2010b). Such findings further mark cyanobacteria as promising feedstock for biodiesel production.

Besides microalgae and cyanobacteria, other oleaginous unicellular microorganisms including bacteria, filamentous fungi, and yeasts have also been utilized for biodiesel production under the same brand of “third generation biodiesel”. Yeasts not only sustain the unique features of microalgae, such as high lipid, accumulation of 30% dry wt. (Singh et al., 2007), but also can be genetically modified to enhance production (Li and Jiang, 2013), and 38.2% for Synechococcus sp., are known to have the highest capability to accumulate oil (Beppou et al., 2011).

2.2. Mainstream strategies

Conventionally, biodiesel is produced through the agitation of the reagents, i.e., oil, alcohol (mainly methanol), and catalyst at about 60 °C (just below the boiling point of methanol i.e. 64.7 °C) for around 1 h. Currently, the majority of industrial biodiesel production practices worldwide are batch or continuous processes with mechanical agitation (Noipin and Kumar, 2014). The co-solvents used should 1) improve the conventional impeller agitation systems (Hosseini et al., 2014). For instance, Hosseini et al. reported a reactor equipped with a helical ribbon-like agitator using which at 900 rpm stirring speed and after 20 min residence time, 97.3% conversion of triglycerides to methyl esters was achieved. They argued that based on the experimental results, the transesterification with ultrasound irradiation could change the biodiesel density by about 0.3 kg/m³; the viscosity by 0.12 mm²/s; the pour point by about 1-2 °C, and the flash point by 5 °C compared to the traditional method (Sajjadi et al., 2015).

Separation of biodiesel and glycerin, the main by-product of the transesterification reaction, is a slow process and is usually achieved by gravitational settling. This could lead to longer operating times, bigger equipment and larger amount of steel and consequently increased production cost (Shirazi et al., 2013b). Therefore, acceleration of glycerol/biodiesel decantation could play an important role in the overall biodiesel refinery process. In a recent study, Shirazi et al. (2013b) reported the application of NaCl-assisted gravitational settling as an economizing strategy. They argued that the addition of 1 g conventional NaCl salt/100 ml glycerol–biodiesel mixture decreased the glycerol settling time significantly by 100% while maintaining the methyl ester purity as high as the conventional (10 g NaCl). In a different study, Noureddin et al. (2014) investigated the interactive effects of prominent parameters, i.e., temperature (25-65 °C), NaCl addition (0-2 g/100ml), and methanol concentrations (10-30 vol.%) on decantation behavior of glycerol/biodiesel mixture. They reported that decantation time was significantly decreased by 200% (3 min) under the optimum conditions, i.e., 45 °C, 1 g NaCl addition and 20% excess methanol (Noureddin et al., 2014). Electrocoagulation at high voltages could also significantly accelerate the decantation rate (Tabatabaei and Khatamifar, 2009). As mentioned earlier, membrane reactors could integrate both reaction and separation stages, eliminating the downstream biodiesel/glycerin separation stage. Stand-alone membrane modules could also be used in order to separate glycerin from biodiesel after the termination of the reaction. In a study, the authors claimed that the synthesized solvent resistant nanofiltration (NCSM) membranes achieved excellent glycerol removal up to 100% glycerol rejection without significant decline in flux permeation. Moreover, the presence of MWCNs in the PI membrane structure resulted in enhanced chemical and thermal resistance as a result of polymer chains of different hydrophobic characters mobility limitation. They also stated that the antifouling properties of the modified membranes were improved compared to the neat PI membrane (Peyravi et al., 2015).

2.3. Downstream strategies

Innovative downstream strategies basically deal with 1) separation of biodiesel and glycerin, 2) purification of biodiesel and glycerin, and also 3) improving the characteristics of the produced fuel.

2.3.1. Biodiesel-glycerin separation (decantation)

The presence of MWCNTs in the PI membrane structure resulted in enhanced chemical and thermal resistance as a result of polymer chain mobility limitation. They also stated that the antifouling properties of the modified membranes were improved compared to the neat PI membrane (Peyravi et al., 2015).
2.3.2. Biodiesel purification

Biodiesel should undergo a purification step in order to meet the ASTM D6751 or EN 14214 quality standards for biodiesel (B100). Purification of biodiesel is conventionally carried out by wet and/or dry washing. These processes along with the novel purification methods such as membrane separation technology (MST) and extraction by ionic liquids have been well reviewed very recently by Stojković et al. (2014). In their comprehensive review, they highlighted the existing controversial observances in the literature on the purification efficiency (refining yield, fuel properties, and the fulfillment of prescribed standard limits) of wet and dry washing and suggested that various purification methods need to be evaluated for their real purification efficiency under identical conditions (Stojković et al., 2014).

2.3.3. Biodiesel wastewater treatment

Nevertheless, since currently water washing is the most widely used process in industrial-scale biodiesel refineries; therefore, treating the huge amount of highly polluting wastewater generated on a daily basis (3–10 L water/L biodiesel; COD, 35000 mg/L; BOD, 29000 mg/L) is of critical importance. Recently, Shirazi et al. (2013c) applied commercial electrospun polysulfone membrane for treatment of biodiesel wastewater and achieved promising reduction rates of 75%, 55%, 92%, 96%, and 30% for COD, BOD, TS, TDS, and TSS, respectively. Using a different approach, Pitakoolnil and Hunsom (2014) used commercial chitosan flakes to treat biodiesel wastewater through absorption. They reported that by a single adsorption within 3 h in the presence of 3.5 g chitosan/L at a mixing rate of 300 rpm, BOD, COD, and oil & grease were reduced by 59.3%, 87.9%, and 66.2%, respectively. They also indicated that repetitive adsorption for four times using fresh flakes further enhanced the removal of BOD, COD, and oil & grease up to 93.6%, 97.6%, and 95.8%, respectively. Their findings could have been more promising if the commercial chitosan used could be regenerated. However, the NaOH-regenerated chitosan sustained only 40% of its adsorption capacity (Pitakoolnil and Hunsom, 2014). Therefore, commercial electrospun polysulfone membranes seem to comparatively hold greater promises for industrial-scale applications given their availability and relatively low cost.

2.3.4. Glycerin purification

Glycerin could also be purified and sold as a strategy to economize the whole production process (Hasheminnejad et al., 2011). Among the methods currently used for glycerol purification are MST and distillation (Javani et al., 2012). MST is more cost-effective than distillation (Hasheminnejad et al., 2011). Among the methods currently used for glycerol purification are MST and distillation (Javani et al., 2012). MST is more cost-effective than distillation (Hasheminnejad et al., 2011). Among the methods currently used for glycerol purification are MST and distillation (Javani et al., 2012). MST is more cost-effective than distillation (Hasheminnejad et al., 2011). Among the methods currently used for glycerol purification are MST and distillation (Javani et al., 2012). MST is more cost-effective than distillation (Hasheminnejad et al., 2011).

2.3.5. Alcohol recovery (recycling)

One of the downstream strategies usually neglected is the recovery/recycling of the excess alcohol (mostly methanol) fraction from both biodiesel and glycerin. In fact, due to the reversible nature of the transesterification reaction, excess alcohol is mostly used to drive the reaction towards the final product, i.e., biodiesel. Under conventional transesterification conditions, i.e., methanol to oil molar ratio of 6:1, the recoverable methanol from biodiesel and glycerol are around 2% and 25%, respectively (Mythili et al., 2014). Therefore, inclusion of this downstream strategy could significantly influence the economic viability of the process.

On the other hand, it should be noted that the presence of excess methanol and its progressive evaporation generally affects the decantation time negatively through the formation of miniemulsions (Noureddin et al., 2014). More specifically, methanol is adsorbed at the interface between the glycerin and biodiesel phases and consequently reduces the interfacial tension (IFT). In better words, the adsorbed molecules of methanol would form a mechanically strong and elastic interfacial film that would act as a barrier against aggregation and coalescence (Mythili et al., 2014). However, if the excess methanol exceeds a certain level, the surplus obviously enters the glycerin phase more than the biodiesel phase due to the fact that there are extensive possibilities for hydrogen bonding between the glycerin molecules and methanol. The contained methanol in the glycerol phase would result in decreased viscosity of glycerin which consequently facilitate its speedy decantation (Noureddin et al., 2014). The exact amount of the excess alcohol to be used in the process in order to accelerate the glycerin-biodiesel decantation process needs to be determined according to a specific biodiesel production practice. Such strategy would be logical only if downstream recovery of methanol from biodiesel and glycerin has been implemented and that the production system is well contained to prevent leakage of the methanol vapor.

2.3.6. Biodiesel additives

A post-production strategy which could potentially enhance the economic viability of the whole production cycle through value addition to biodiesel or its blends is to improve biodiesel properties, engine performance, and exhaust emission characteristics. Various types of additives such as oxygenated additives (Ribeiro et al., 2007), antioxidants (Hajari et al., 2014), cetane number improvers (Venkateswarlu, 2015), lubricity improvers (Anastopoulos et al., 2001), cold flow improvers

![Graph](https://example.com/graph.png)
(Mohammadi et al., 2014), and combustion improvers (Sadik Basha and Anand, 2012; Kannan et al., 2011; Mirzajanzadeh et al., 2015) are used in biodiesel to meet specification limits and to enhance quality. In a very recent study, Mirzajanzadeh et al. (2015) introduced a novel soluble hybrid nanocatalyst as a promising combustion improver. The hybrid nanocatalyst containing cerium oxide on amide-functionalized MWCNT (CeO$_2$-MWCNTs), owing to the high surface area of the soluble nano-sized catalyst particles and their proper distribution along with catalytic oxidation reaction, resulted in significant overall improvements in the combustion reaction specially in B20 containing 90 ppm of the catalyst B20(90 ppm). More specifically, all pollutants, i.e., NO$_x$, CO, HC, and soot were reduced by up to 18.9%, 38.8%, 71.4%, and 26.3%, respectively, in B20(90 ppm) compared to neat B20. The innovated fuel blend also increased engine performance parameters, i.e., power and torque by up to 7.81%, 4.91%, respectively, and decreased fuel consumption by 4.50% (Fig. 1) (Mirzajanzadeh et al., 2015). The authors concluded that the unique oxygen donation/absorption properties of CeO$_2$ resulted in CO oxidation reaction. They also stated that CeO$_2$-nano particles owing to their decreasing impact on peak temperature in the combustion chamber led to decreased production of nitrogen oxides (NO$_x$) (Mirzajanzadeh et al., 2015).

4. Concluding remarks

Despite decades-long research conducted on various aspects of biodiesel production in order to improve the economic viability of this unique renewable energy carriers, its future sustainability remains uncertain. This is mainly ascribed to the insufficient oil feedstock available to meet the growing demands for biodiesel, and on the other hand, the controversial food vs. fuel crisis. Moreover, given the recent falling oil prices, maintaining biodiesel’s market price competitive to that of petroleum-derived diesel will be a challenge as well. In line with these points, enhancing the economic aspects of biodiesel production through integrated strategies targeting different stages (i.e. upstream, mainstream, and downstream) is vital (Fig. 2).
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