Short Communication

Biodiesel wash-water reuse using microfiltration: toward zero-discharge strategy for cleaner and economized biodiesel production

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HIGHLIGHTS

- A simple but economically feasible refining method to re-use biodiesel wash-water.
- Standard-quality biodiesel was obtained using the proposed strategy.
- Up to 15\% less water consumption after two rounds of biodiesel production operations.
- Strengthening the environmental-friendly aspects of biodiesel production process.
- Considerably less wastewater generation toward zero discharge-based operation.

GRAPHICAL ABSTRACT

1. Introduction

Today, the world is faced with three major global concerns, i.e. fresh water shortage (Shirazi et al., 2013a), energy demand (Shirazi et al., 2013b) and environmental pollutions (Shirazi et al., 2013c). Concerning the last two issues, increasing demands and soaring prices of conventional energy carriers e.g. crude oil as well as the global warming phenomenon triggered by greenhouse gas emissions are the key factors which have led to a widespread search for alternative energy resources (Atadashi et al., 2011a). Among various proposed renewable energy resources including solar and wind energies, the most promising choice for the transportation sector is still biofuels e.g. bioethanol, biodiesel, biogas, etc. (Hasheminejad et al., 2011).

In the last few years, biodiesel has been put forth as an environmental friendly alternative to the large volume of petro-based diesel burnt daily (Oh et al., 2012). Biodiesel also known as fatty acid methyl or ethyl ester could be derived from vegetable oils, animal fats as well as waste cooking oil (WCO) through a number of methods and in particular transesterification reaction (Leung et al., 2010; Talebsaei-Kiakalaieh et al., 2013). Similar to the other fuel production processes, refinery i.e. separation and purification, is considered as one of the most important steps in biodiesel production as well. In another word, as the obtained biodiesel is crude and contains several impurities such as glycerol (the main co-product), un-reacted oil, catalyst, excess alcohol, and water, therefore, it should be purified prior to any standard applications.

A number of methods have been used for biodiesel refinery so far such as wet washing, dry washing, and membrane-based technologies (Atadashi et al., 2011b; Shitt et al., 2012; Shirazi et al., 2013b); however, water washing of biodiesel is still regarded as the most common biorefinery method for cleaning biodiesel worldwide (Ma and Hanna, 1999; Van Gerpen, 2005). During this process, for each L of biodiesel 3-10 L of hot water (50 to 60°C) is used to remove the impurities from fatty acid methyl or ethyl ester phase. In better words, this could result in the generation of about 3 to 10 L of highly organic wastewater, namely biodiesel wash-water. Therefore, one of the today’s most challenging and also neglected aspects of biodiesel production is the high volume of this highly polluting saponified effluent with high pH, BOD and COD values.

Biodiesel was produced based on the standard method for transesterification of WCO as described by Mohammadi et al. (2013). Then, pre-heated deionized water (60°C) was added to the crude biodiesel (1:1) and the mixture was agitated gently, then left to settle overnight. The process was followed by the separation and discharge of the saponified effluent (i.e. the lower and polar phase). This procedure was repeated three times for more efficient purification, and all the obtained batches of the generated wash-water were mixed and stored at 4°C until use.

The hybrid filtration procedure and the four configurations used for treatment of water-washing effluent is shown in Figure 1. The treated effluent samples (C1, C2, C3 and C4) were then re-used for washing a crude biodiesel and the purity of the washed and dried biodiesel (for 48h at 80°C) was measured by Gas Chromatography (GC). Finally, the effluent which led to the highest biodiesel purity was selected and diluted at different ratios with deionized water (DW) and the water-washing step of crude biodiesel was repeated.

2. Material and method

2.1. Materials and chemicals

Biodiesel was produced from WCO obtained from a local restaurant, and using analytical grade methanol and potassium hydroxide (Merck, Germany) as reaction agents. Deionized water (Milli-Q, Millipore, USA) was used for water-washing experiments. Commercial polypropylene (PP) microfilters (So~Pure, Korea) with 1 and 5 µm pore sizes as well as commercial active carbon (AC) and sand filter cartridges were used in the hybrid modules.
2.3. Analysis

Wash-water samples, before and after filtration, were analyzed for chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS) and total suspended solids (TSS) based on the standard methods (American Public Health Association, 1995). The methyl ester yield (purity), after water-washing was measured based on the method described in our previous work (Shirazi et al., 2013b).

3. Results and discussion

As mentioned earlier, the effluent generated during water-washing of biodiesel is a highly polluting saponified wastewater which should be treated prior to disposal. Table 1 presents the characteristics of the wash-water effluent investigated in the present study. Given the high COD and BOD values, the necessity to implement environmental-friendly strategies to first reduce the overall volume of such wastewater during industrial activities and second to treat it is obvious. Therefore, provided that the impurities contained in the effluent could be partially removed, then it would be feasible to re-use the wash-water effluent as it is, or in a diluted form by mixing it with clean water at an optimum ratio. Achieving either of those could lead to a significant reduction in the fresh water volume consumed during the production process and consequently the waste water generated.

Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>TDS (mg/L)</th>
<th>TSS (mg/L)</th>
<th>COD (mg O₂/L)</th>
<th>BOD (mg O₂/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>840</td>
<td>440</td>
<td>35600</td>
<td>30500</td>
</tr>
<tr>
<td>C 1</td>
<td>750</td>
<td>130</td>
<td>29020</td>
<td>26700</td>
</tr>
<tr>
<td>C 2</td>
<td>750</td>
<td>210</td>
<td>29610</td>
<td>27700</td>
</tr>
<tr>
<td>C 3</td>
<td>750</td>
<td>190</td>
<td>29820</td>
<td>27900</td>
</tr>
<tr>
<td>C 4</td>
<td>750</td>
<td>370</td>
<td>29840</td>
<td>28100</td>
</tr>
<tr>
<td>D 1</td>
<td>440</td>
<td>240</td>
<td>19300</td>
<td>16900</td>
</tr>
<tr>
<td>D 2</td>
<td>360</td>
<td>200</td>
<td>14530</td>
<td>12200</td>
</tr>
<tr>
<td>D 3</td>
<td>240</td>
<td>80</td>
<td>8810</td>
<td>7100</td>
</tr>
</tbody>
</table>

D1: 30% distilled water (DW) and 70% wastewater (WW)
D2: 50% of DW and 50% of WW
D3: 70% of DW and 30% of WW

In light of that, in the first and second configurations used in this study (C1 and C2, respectively), the treatments were carried out by a PP filtration (1 and 5 µm pore size, respectively), followed by sand filtration and AC application. In the third and fourth configurations (C3 and C4, respectively), the AC stage was eliminated. Table 1 tabulates the impact of each treatment configuration on reducing pollution indices in particular COD and BOD values. The effluent generated in this work possessed the COD and BOD values of 35600 and 30500 mg O₂/L, respectively. After treatments, the highest COD and BOD reduction rates were obtained using the first configuration (C1) (around 18.5 and 12.4%, respectively). C1 also led to the highest TSS reduction as well. Nevertheless, the concentrations of impurities in all the treated effluents including that of the C1 were still higher than the standards values (50 mg/L and 250 mg/L for BOD and COD, respectively) and therefore their disposal would not be safe environmentally.

To address this challenge, we tried to implement a strategy i.e. complete or partial re-use of the treated wash-water for further water-washing of crude biodiesel. In fact, the crude biodiesel was washed by the treated effluents and the purity of the final biodiesel products were measured by GC analysis. Biodiesel samples washed using DW and un-treated wastewater (WW) were also used as controls (A and B, respectively). Moreover, C1-treated effluent (due to its best post-treatment quality) was also diluted with DW at different ratios (D1: 30% DW and 70% WW; D2: 50% DW and 50% WW; and D3: 70% DW and 30% WW). Obviously dilution led to reduced COD and BOD indices of the wash-water (Table 1).

Clearly, the yield extremes (ester contents) of 98.51 and 80.55% belonged to biodiesel products washed by DW and WW (Table 2). The minimum ester content required to meet EN14214 is defined at 96.5% which was only achieved when C1 wash-water was diluted with 70% DW i.e. D3. By comparing the four treatment configurations in terms of the impact the treated wash-waters on the purity of the final biodiesel product, the role of pore size and activated carbon in achieving higher purity values is also clear. In another word, the application of 1µm-filtration and activated carbon (as in C1) resulted in the highest biodiesel purity at 93.08%.

Table 2.

Methyl ester yield (ester content) of the products washed with different types of water.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield of methyl esters (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>98.51</td>
</tr>
<tr>
<td>B</td>
<td>80.55</td>
</tr>
<tr>
<td>C1</td>
<td>93.08</td>
</tr>
<tr>
<td>C2</td>
<td>91.93</td>
</tr>
<tr>
<td>C3</td>
<td>87.89</td>
</tr>
<tr>
<td>C4</td>
<td>83.59</td>
</tr>
<tr>
<td>D1</td>
<td>93.56</td>
</tr>
<tr>
<td>D2</td>
<td>94.88</td>
</tr>
<tr>
<td>D3</td>
<td>96.52</td>
</tr>
</tbody>
</table>

A: Biodiesel washed by DW
B: Biodiesel washed by WW

Overall, the findings of the present study revealed that depth-filtration-based microfiltration and 70% dilution rate with fresh water (Figure 2) not only achieved standard quality biodiesel product but also led to 15% less water consumption after two rounds of production operations. In better words, it is advisable that industrial-scale biodiesel production plants use clean water for washing the first product batch and apply the simple procedure offered herein for performing the washing stage of the succeeding product batch (Fig. 2). This would be translated into a considerable reduction of up to 15% in the total volume of fresh water used during the operation process. Furthermore, it would strengthen the environmental-friendly aspects of the biodiesel production process for wastewater generation is obviously cut by the same rate as well.

Fig.2. General scheme of the proposed biodiesel production process with an emphasis on biodiesel wash-water reuse.
4. Conclusion

PP-based microfiltration (1 µm pore size), followed by sand and activated carbon separations and in combination with 70% dilution rate with fresh water enabled re-use of biodiesel wash-water while still led to standard-quality biodiesel product. Generally speaking, the procedure offered herein resulted in up to 15% less water consumption and clearly less wastewater generation, meaning more environmental-friendly biodiesel production operation. Furthermore, the findings of the present study could be further investigated as an economizing strategy for biodiesel production.

References