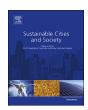
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Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel



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ABSTRACT

Biodiesel production from waste oils is an attractive option to produce biodiesel economically, but high free fatty acids (FFA) in waste oils are a serious bottleneck for the process of transesterification. Present investigation deals with the utilization of waste cooking oil (WCO) for the production of biodiesel. The acid value of WCO was 5.5 mg KOH/g which indicated high FFA content. The WCO was subjected to esterification using different acid catalysts (HCl, $\rm H_2SO_4$ and $\rm H_3PO_4$) and $\rm H_2SO_4$ catalyzed reaction was found to be the most efficient since the FFA reduced up to 88.8% at 60 °C with 1:2.5 methanol to oil molar ratio. Transesterification was done in the presence of alkali catalyst (KOH) and Fatty acid methyl ester (FAME) yield was 94% in the presence of 1% catalyst at 50 °C. The biodiesel was characterized based on acid value, saponification value, iodine value, cetane number, specific gravity, viscosity, cloud point, pour point and calorific value. The Gas Chromatography (GC) analysis of synthesized biodiesel was also performed. Base on ASTM standards, alkali catalyzed transesterification was an efficient method to produce biodiesel form WCO. Results revealed that the waste cooking oils can be converted into biodiesel as an energy source along with environmental pollution reduction.

1. Introduction

The energy demand is continuously increasing due to fast industrialization and metropolitan growth. The major energy resources are petroleum, coal and natural gas and due the non-renewable nature, these energy sources are decreasing day by day (Arshad et al., 2018). Recently, the petroleum prices have been setting record high in the history due to heavy dependence on petroleum as a major source of fuel for transportation and electricity generation. On the other hand, the exploitation of these conventional energy resources is also a reason of global warming, which needs to be tackled by adopting alternative energy sources (Canesin & Oliveria, 2014). Both energy and environmental deterioration are serious crisis, which could possibly be reduced by adopting alternative energy sources such as biofuels generation from renewable sources as well as the adoption of sustainable and environmental friendly methods for the generation of biodiesel (Asri & Sari,

2015; Asri, Sari, Poedjojono, & Suprapto, 2015; Haigh, Abidin, Saha, & Vladisavljević, 2012; Hiwot, 2017; Noiroj, Intarapong, Luengnaruemitchai, & Jai-In, 2009; Saifuddin, Raziah, & Farah, 2009; Omar, Nordin, Mohamed, & Amin, 2009; Wang, Ou, Liu, Xue, & Tang, 2006).

Biofuels are very attractive option to overcome the energy crisis since waste feedstock's are available freely for the production of biofuels (biodiesel, bioethanol, biogas etc) by different chemical and biological conversion technologies (Che, Sarantopoulos, Tsoutsos, & Gekas, 2012; Wen, Jiang, & Zhang, 2009). The biofuel production is increasing globally, which will grow in coming years due to continuous dwindling of fossil fuel reserves (Yusuf, Kamarudin, & Yaakub, 2011). Among different types of biofuels, biodiesel is getting more attraction in view of properties and chemical nature, which can be used as blend with diesel fuel (Nisar et al., 2018). To utilize the biodiesel as a fuel, no engine modification is required for (Boon, Van Dijk, De Munck, & Van

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Den Brink, 2011) and in contrast to conventional petroleum diesel, the biodiesel is a clean, safe and non-hazardous due to its biodegradability, renewable and carbon neutral nature (Dong, Zhu, & Dai, 2012; Roy, Wang, & Alawi, 2014). Chemically, biodiesel is fatty acid methyl esters (FAME), which can be synthesized by chemical reaction between alcohol and oil in presence of a suitable catalyst, and feedstock's like energy cops, animal fats, kitchen wastes, insects and microalgae can be used for the production of biodiesel (Yaakob, Mohammad, Alherbawi, Alam, & Sopian, 2013). To date, the major obstacle in the commercialization of biodiesel is the cost of production. In this regard, the exploitation of waste materials for the production of biodiesel might be useful to reduce the feedstock cost, which makes the process economical. The WCO is a waste, which can be converted into biodiesel and this will be helpful for the reduction of pollution since WCO is wasted into the environment. Secondly, the conversion of WCO into biodiesel will be a valuable addition of energy in existing energy grid (Arshad et al., 2018; Tangy, Pulidindi, & Gedanken, 2016). Moreover, under the current scenario of environmental pollution (Chham et al., 2018; Ghezali, Mahdad-Benzerdjeb, Ameri, & Bouvakoub, 2018; Ibisi & Asoluka, 2018; Mansouri et al., 2018; Mehta, Chandra, Mehta, & Maisuria, 2018; Ramdani, Benouis, Lousdad, Hamou, & Boufadi, 2018), there is need to adopt the clean and green processes as well as methodology. Various researchers studied different feedstock in order to convert free fatty acids (FFA) into methyl ester i.e., Che et al. (2012) used olive pomace oil for the production of FAME BY acid esterification process using sulfuric acid as a catalyst. They observed 50% reduction in FFA values at low methanol to oil ratio and over 80% reduction for high methanol to oil ratio. Similarly, Ouachab and Tsoutsos (2013) also studied the transesterification of olive pomace oil and achieved the FAME yield of 97.8%. Chai, Tu, Lu, and Yang (2014) also converted vegetable in to FAME and it was found that the 19.8:1 methanol to oil molar ratio worked well only within the FFA range of 15-25%, while the suggested 5% sulfuric acid worked well only within the FFA range of 15–35%. The FAME yields were 83.08%, 88%, 90%, 91.7%, 97.8% and 94% and 81.3% for the waste cooking oils using different catalyst (Table 1). So far, these studies revealed that WCO can be converted into FAME (Asri & Sari, 2015; Asri et al., 2015; Haigh et al., 2012; Noiroj et al., 2009; Saifuddin et al., 2009; Omar et al., 2009; Wang et al., 2006). This technique have been also employed for the production of biodiesel from non-cooking oils i.e., Mumtaz et al. (2016) utilized Eruca sativa oil for the production of biodiesel by Novozyme-435 lipase and Aspergillus niger lipase catalyzed transesterification. The biodiesel production was recorded 98.3% and 56.4% for oil catalyzed by Novozyme-435 and Aspergillus niger lipase, respectively. Similarly, animal bones modified with potassium hydroxide (KOH) as heterogeneous solid base catalyst for transesterification of non-edible Jatropha oil was used and FAME yield of 96.1% was achieved. Nisar et al. (2018) used *Brassiceae* family plants oil for biodiesel production using chemical refining followed by direct homogeneous alkali catalyzed transesterification and methyl esters from *Brassiceae* family plants are acceptable biodiesel.

Waste cooking oil (WCO) is easily available from restaurants, cafeterias and household kitchens. Present research was focused on the conversion of WCO into biodiesel. The high level FFAs in waste cooking oils result in accelerating some undesirable side reactions during biodiesel production. Therefore, WCO was pretreated first with mineral acids for reduction of FFAs and then subjected to transesterification in the presence of base as a catalyst. The synthesized biodiesel was characterized and compared with fuel standards.

2. Material and methods

The WCO was collected from student cafeteria in the PARS campus, University of Agriculture, Faisalabad. Initially, the oil was filtered to remove all the insoluble impurities and heated at 100 °C to remove moisture. All the chemicals used were of analytical grade and purchased from Sigma-Aldrich, except as noted otherwise.

2.1. Pretreatment of WCO

Pretreatment of WCO was done as reported elsewhere (Chai et al., 2014). For treatment, three neck reactor (250 mL) equipped with reflux condenser was used to avoid alcohol vaporization. The reaction contains 50 mL WCO, 10 mL methanol and 0.2% acid catalyst. The reaction mixture was fed into batch reactor and experiment was conducted at 50 °Cfor 6 h. Mineral acids (HCl, H₂SO₄ and H₃PO₄) were used for pretreatment. After stipulated time period, the samples were withdrawn and centrifuged. The methanol layer was drained off and the WCO was collected and washed with deionized water three times. The water content was removed by vacuum evaporation and the FFAs values were determined. Influencing parameters (methanol to oil ratio, catalyst dose, reaction time and temperature) were optimized and the FFA was calculated using the relation shown in Eq. (1).

Free fatty acid conversion (%) =
$$\frac{A_i - A_t}{A_i} \times 100$$
 (1)

Where, A_i and A_t , refer to the acidity (at zero and time t).

2.2. Trans-esterification of pretreated WCO

KOH was mixed with methanol in a three neck batch reactor $(250\,\mathrm{mL})$ equipped with reflux condenser. The esterified oil was added in batch reactor and the reaction mixture was heated at required

Table 1Literature survey of different processes used for the conversion of oils into biodiesel.

S. No	Feedstock	Catalysts	FAME Yield	Ref.
1	Waste cooking oil	CaO/KI/γ-Al ₂ O ₃	83.08 %	Asri et al. (2015)
2	=	Lipase	88 %	Saifuddin et al. (2009)
3	=	H_2SO_4	90%	Wang et al. (2006)
4	=	KOH/Al ₂ O ₃	91.7%	Noiroj et al. (2009)
5	=	CaO/KI/γ-Al ₂ O ₃	83%	Asri and Sari (2015)
6	=	Acid-based catalyst	97.8%	Ouachab and Tsoutsos (2013)
7	=	Purolite D5081	94%	Haigh et al. (2012)
8	=	Novozyme 435	90%	Haigh et al. (2012)
9	=	H ₂ SO ₄	80% FFA reduction	Che et al. (2012)
10	=	Ferric suphate + acid catalyzed	81.3%	Omar et al., 2009
11	=	Acid catalyzed	FFA reduction	Chai et al. (2014)
12	=	КОН	94%	Present study
	Non cooking oil	Novozyme-435	98.3%	Mumtaz et al. (2016)
13	=	Aspergillus niger	56.4%	Mumtaz et al. (2016)
14	=	KOH/calcined waste animal bones	96.1%	Nisar et al., 2017
15	=	Acid	96%	Kombe et al. (2012)
16	=	Caustic	94%	Kombe et al. (2012)

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