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Journal of Environmental Biology

ISSN: 0254-8704 (Print)
ISSN: 2394-0379 (Online)
CODEN: JEBIDP

Purification and characterization of waste stream glycerol derived from biodiesel industry

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Publication Info

Paper received:
20 September 2015

Revised received:
05 May 2016

Accepted:
24 August 2016

Abstract

Biodiesel possesses the record of mostly investigated eco-friendly biofuels, which can be fashioned by transesterification of natural fatty acids. Large volume of waste stream glycerol is generated as a byproduct during the production of biofuel. Disposal of this glycerol without proper treatment in the environment is hazardous as it contains copious impurities like methanol, organic salts, free fatty acids and water. Alternatively, waste stream glycerol can be utilized as cheap carbon source for the production of high-value chemicals like ethanol, citric acid, propanediol etc. In this study, waste glycerol was partially purified to increase its concentration by sequential steps like distillation, acidification and adsorption process to utilize it effectively as carbon source for the microorganisms. The concentration of acidified glycerol treated with sulphuric acid was found to be high when compared with phosphoric acid. The glycerol rich phase was high in phosphoric acid and GC-MS studies also reveal that the phosphoric acid removes major impurities when compared with sulphuric acid. The purified glycerol obtained could be stored and used as a carbon source for the production of high value chemical.

Key words

Acidification, Bio-fuel, Distillation, Waste stream glycerol

Introduction

The anticipated global energy will be 50% more than today's requirement in 2030 (Bhaskar *et al.,* 2014). The energy crisis is a major problem focused throughout the world due to excessive utilization of fossil fuels. The world economy depends on the transportation sector, which consumes 96% of the fossil fuel energy (Yahaya *et al.,* 2014). Combustion of fossil fuels from vehicles emits carbon dioxide along with hydrocarbons, particulate matter, carbon monoxide, oxides of nitrogen and other carcinogens that pose direct and indirect intimidations to mankind and ecosystems (Schiermeier *et al.,* 2008). Alternative and renewable energy sources have become more conspicuous in recent years due to above stated issues (Noshadi *et al*., 2012). Among other renewable energy resources, biodiesel has gained substantial interest all over the globe due to its properties like biodegradability and less exhaust gas emission (Chozhavendhan *et al.,* 2015a). The increase in biodiesel production inevitably increases the production of coproduct glycerol. Approximately, 0.1kg of waste stream of glycerol is produced for every 1kg of biodiesel production (Chozhavendhan *et al*., 2015b). Waste stream glycerol usually contain low concentrated glycerol (Leung *et al.,* 2010; Priscilla *et al*., 2009; Escapa *et al.,* 2009) and because of dropped market value it is usually disposed as a waste stream from small scale industries due to expensive and extensive process of purification (Johnson and TaconiKa 2007). Utilization of waste stream glycerol is of great

importance for sustainable headwayof biodiesel industry and for environmental concerns. Pure glycerol has wide application in food or pharmaceutical industries. High energy content of glycerol has attracted the researcher all over the world to investigate the bioconversion of glycerol for high-value chemicals such as ethanol, succinic acid, citric acid, DHA etc. (Chozhavendhan *et al.,* 2014). Conversely, existence of colossal amount of impurities like methanol, free fatty acids, salt, soap, ash etc., (Ngo TA *et al.,* 2011, Selembo PA *et al*., 2009) has made the waste stream glycerol not to be directly used in the industries for its application. As per current scenario, the purification or separation of glycerol-rich phase is necessary for utilization of waste stream glycerol as a cheap substrate for the production of higher value chemicals in large-scale industrial use (Christy Mathelin *et al*., 2015). In light of the above, the present study investigated various impurities present in the waste stream glycerol and its elimination from the sample by various simple methods of purification of waste stream glycerol. The concentration and characterization of glycerol-rich phase or acidified glycerol from crude glycerol were characterized by GC-MS and GC-FID.

Materials and Methods

Sample collection : Availability of waste stream glycerol round the year has encouraged the researchers to work on it. The waste glycerol was obtained from biodiesel production unit located in Bannari Sugar Pvt. Ltd., Sathyamangalam, Tamil Nadu. The waste stream glycerol was dark brown in colour with pH 9.6 and high viscous fluid obtained from a single batch was used throughout the study. Other chemicals used in the study were of analytical grade.

Purification process of waste streams glycerol : Biodiesel derived waste stream glycerol was semi-solid crude at room temperature. The sample was warmed at 50°C to make it highly viscous fluid. Initially, methanol was removed from 800g of waste stream glycerol sample by placing in simple distillation at 65°C for 30 min. The molten waste stream glycerol of 200 g was acidified with two different sulphuric acid and phosphoric acid, with a constant volume of acid under gentle stirring. The mixture was left static in a separating funnel until the phase separation of three distinct layers was formed. Free fatty acid at the top layer, glycerol rich phase in the middle layer and inorganic salts at the bottom layer were formed in the separating funnel. The middle glycerol-rich layer was separated after simple decantation and filtration from the separating funnel. To decolorize the extracted acidified glycerol, sample was mixed with 1% activated charcoal at 200 rpm for 1 hr and then filtered by Whatman filter paper (no1). Glycerol-rich phase after filtration was centrifuged at 8000 rpm for 5 min. to separate the suspended salts and other impurities (Cai *et al*., 2013).

Determination of glycerol concentration by UV-Vis Spectrophotometer method : Glycerol content in the acidified glycerol was estimated by UV- Visible mini Spectrophotometer at 410 nm. UV-VIS spectroscopy gives an idea about the transparency and color of the sample (Paolo *et al.,* 2005). Purification process like distillation and acidification was enough to get glycerol-rich phase, but the color of pure glycerol was white with negligible absorbance in contrary to the acidified glycerol phase. The concentration of decolorized acidified glycerol of two different acids was obtained by plotting the OD value in the standard graph and confirmed the same with GC-FID.

Characterization of glycerol : The nature of waste glycerol and acidified glycerol of different acids were characterized and compared with pure commercial glycerol. Properties such as density, pH, ash content, flash point, fire point, cloud point, pour point, vapour pressure and solubility in water were characterized by the standard methods. The GC-MS studies were carried out to find the impurities present in the waste glycerol and acidified glycerol (Nanda *et al*., 2014).

Results and Discussion

High energy content captivated the use of waste stream glycerol as an alternate substrate for sugar molecule (Zhanyou *et al.,* 2007). Impurities in waste glycerol interact with each other and can have a synergic effect on the bioconversion process (Dorota *et al*., 2014). Initially, purification of waste glycerol was carried out by simple

Table 1 : Effect of different acids in waste glycerol purification

	Sulphuric acid	Phosphoric acid
Distilled waste stream glycerol (g)	200	200
Amount of acid added (ml)	10	10
Phase separation time (min)	150-180	30-45
FFA formation (g)	108	106
Acidified glycerol-rich phase formation (g)	74	84
pH	2.6	4.5
Acidified glycerol remains after centrifuge (g)	64	77

Table 2 : Determination of concentration of different glycerol by GC – FID.

Sample	GC-FID analysis
Concentration of waste stream glycerol (%)	10
Concentration of acidified glycerol by sulphuric acid (%)	32.7
Concentration of acidified glycerol by phosphoric acid (%)	24.9

distillation at 65°C for 30 min to recover methanol necessary for industrial or large scale application. The recovery of non-reactive excess methanol for reusing is an economic way than using a new methanol for the production of biodiesel because recovery of methanol is less cost effective than using new methanol (Bohon *et al*., 2011). The presence of methanol might act as an inhibitory compound to the microbial growth and sometimes produce unwanted byproducts during fermentation (Sneha *et al*., 2009). Disposal of waste glycerol without recovery of methanol might cause environmental concerns. Table 1 compares the effect of different acid during purification of waste stream glycerol with respect to acidified glycerol yield, phase separation time, free fatty acid content, acidified glycerol-rich phase and final yield of acidified glycerol of various acids.

The results revealed that addition of acid reduced the pH of waste stream glycerol from 9.6 to a near acidic pH, which helps the microbes to utilize waste glycerol for bioconversions when added with other nutrients. In acidification process the soluble soap was converted to insoluble free fatty acid which floats at the top layer. The remaining ions coupled with the catalyst used in biodiesel production precipitate and settle at the bottom layer as contaminated salt (Manosak *et al.,* 2011). Phosphoric acid showed a significant result in separation time and glycerol liberation amount and the presence of salt in glycerol-rich phase was also low when compared with sulphuric acids. However, high acidic condition caused by sulphuric acid resulted in low glycerol liberation and may corrodes the reactor. On the contrary, weak acid like HCl may cause difficulties in the separation of final products. Glycerol-rich phase separation from the waste stream glycerol is well in the range of pH 4-6. The light brown color of the acidified glycerol was subjected to an adsorption process with 1% activated charcoal to remove the color.

Estimation of glycerol concentration : The optical density value of the acidified glycerol samples was noted and plotted on the standard graph and the concentration was found to be 31 % on acidified glycerol by sulphuric acid and 24% acidified glycerol by phosphoric acid (Table 2). The UV – VIS spectroscopy nearly showed equal absorbance of the purified glycerol to that of pure glycerol (Nanda *et al.,* 2014). The concentration of different samples was analyzed quantitatively on GC-FID as 32.7% and 24.9% on acidified glycerol treated with sulphuric acid and phosphoric acid, respectively. Christy Mathelin *et al.,* (2015) 76% concentration of pretreated glycerol by a complex purification process. However, initial glycerol concentration depends on the raw material that was used to produce it and varies from plant to plant (Cesar *et al.,* 2013).

Properties of waste glycerol : The properties of waste glycerol, acidified glycerol with different acids and pure glycerol were compared. The dark viscous waste stream glycerol was slowly transformed into straw yellow through a series of purification process. The properties of acidified

Table 3 : Comparing the properties of waste stream glycerol and acidified glycerol treated with different acids with pure glycerol

Properties	Waste stream glycerol	Acidified glycerol by sulphuric acid	Acidified glycerol by phosphoric acid	Pure glycerol
Color	Dark brown	Straw yellow	Straw yellow	Colorless
pH	9.6	2.6	4.5	6.7
Density (kg m^{-1})	1.29	1.23±0.02	1.23±0.02	1.25
Melting point (°C)	18	18	18	18
Boiling point (°C)	290	≥270	≥240	≥170
Freezing point (°C)	<2	<2	<2	<2
Cloud point (°C)	-11	-53.5	-47.3	-42.7
Pour point (°C)	-16	-58.5	-52.3	-47.7
Flash point (°C)	180	177	270	196
Fire point (°C)	211	204	331	230
Vapour pressure kg/cm^2	0.04	0.16	0.082	0.09
Ash content %	11.25%	≤0.2	0.16	0.132
Solubility in water	Miscible	Miscible	Miscible	Miscible

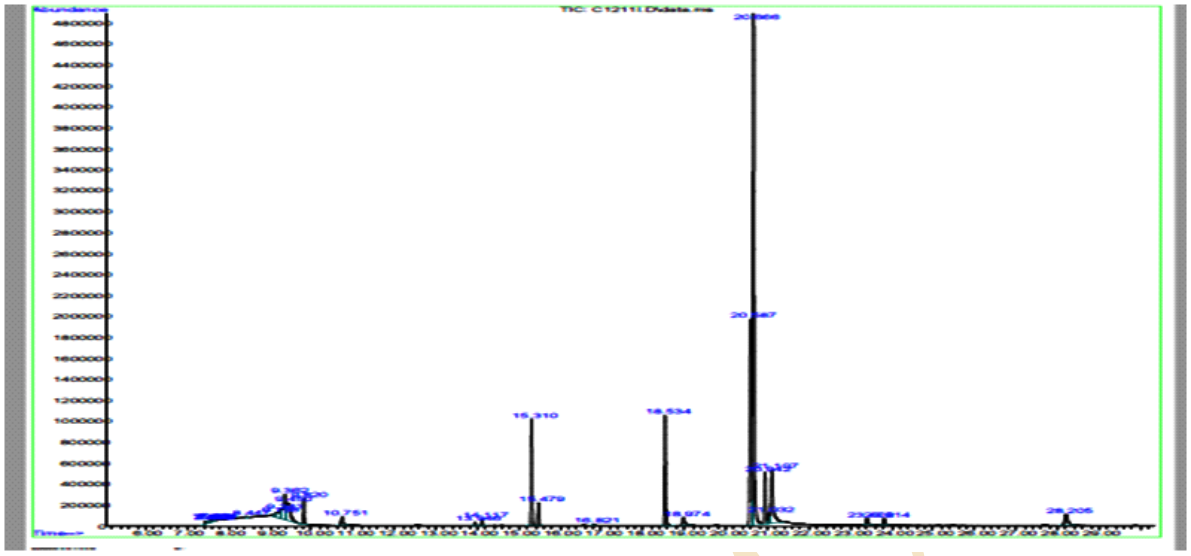

Fig. 1 : GC- MS analysis of waste stream glycerol

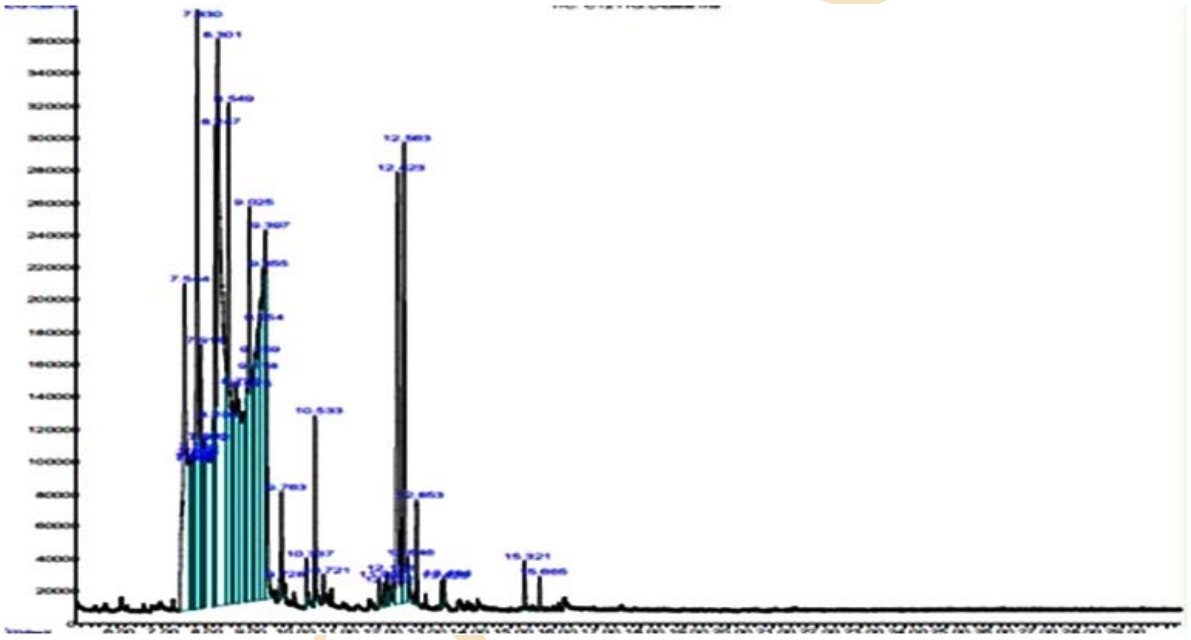

Fig. 2 : GC- MS analysis of *acidified* glycerol treated with sulphuric acid

glycerol with two different acids were compared with pure and waste glycerol as shown in Table 3. The properties of acidified glycerol with phosphoric acid were similar to that of pure glycerol. The too strong acidic action of sulphuric acid gave the final product which was in acid nature, increased in flash and fire point. Though, concentration of acidified glycerol of phosphoric acid was less when compared with sulphuric acid, it showed better result in phase separation, yield and properties similar to pure glycerol. The GC-MS results of waste glycerol, acidified

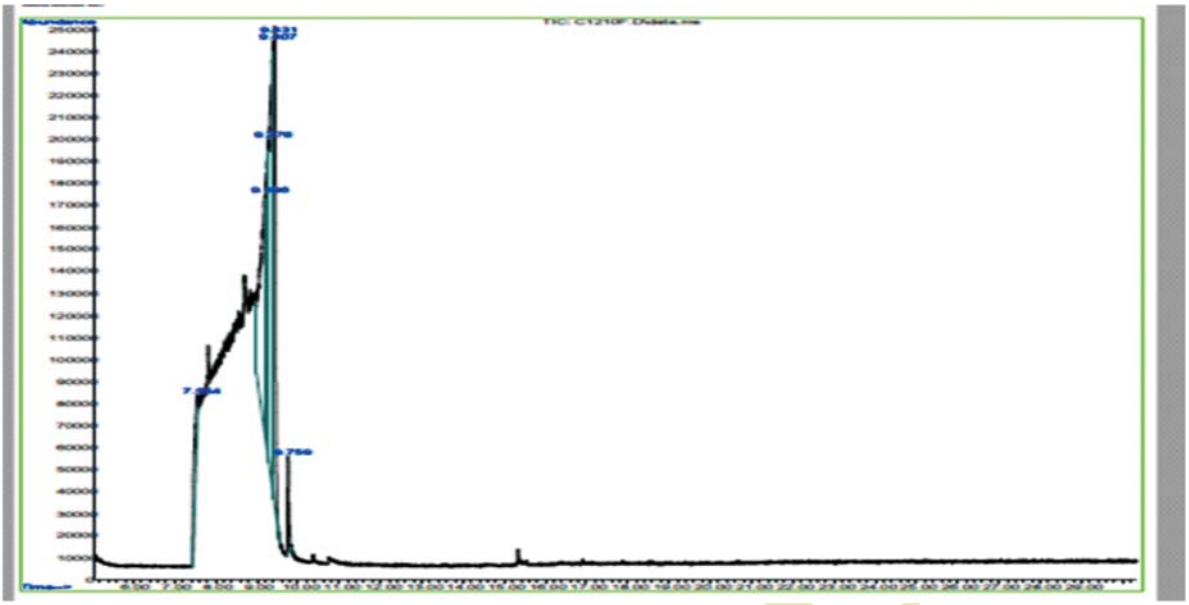

Fig. 3 : GC- MS analysis of acidified glycerol treated with phosphoric acid.

glycerol treated with sulphuric acid and phosphoric acid are depicted in Fig. 1-3. The ninth minute run showed the presence of glycerol and the number of peaks were less in Fig. 3 when compared with Fig. 1 and Fig. 2, which indicates that the impurities were removed by simple purification process. Impurities present in crude glycerol like benzoic acid, methyl ester, acetophenone, decanoic acid, cyclododecanemethanol, 9-octadecenoic acid (Nanda et al., 2014) was removed in phosphoric acid treated glycerol, whereas sulphuric acid reduces only few impurities.

The performance of phosphoric acid was found to be as compared to sulphuric acid in purifying waste glycerol by acidification process. It remove major impurities and maintained the pH in the range of 4-6 which helped the microbes to utilize a carbon source for industrial fermentation process. Phase separation time and liberation of glycerol rich phase from the waste stream glycerol was significant in phosphoric acid when compared with sulphuric acid. Density, viscosity and other physical properties of purified glycerol treated with phosphoric acid were found to be closer to pure glycerol. Purity or concentration of purified glycerol was not up to the mark to find its application in cosmetics or pharmaceutical industries. It can be used as a carbon source for the production value added products. Thus, semi purified glycerol can be stored and used for the biochemical production process.

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