STUDIES ON PURIFICATION OF CRUDE GLYCEROL OBTAINED AS BYPRODUCT FROM BIODIESEL PLANT FOR CONVERSION TO VALUE ADDED PRODUCTS

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Abstract

Crude glycerol is obtained as byproduct from biodiesel production, which accounts for about 10% (by wt) of the biodiesel produced. Glycerol, a byproduct from biodiesel plant has less commercial value and its disposal in environment is hazardous in nature. Conversion of crude glycerol into value added products is also important for economic sustainability of the biodiesel industries. Therefore crude glycerol can be considered as waste organic material with potential to be used as raw material for production of value added products and as a raw material for bio energy production. The composition of crude glycerol varies according to the biodiesel production methods. In order to identify the properties of crude glycerol and the treatment methods to purify it, the characteristics of crude glycerol such as density, alkalinity, ash content, water content were studied. The alkalinity test of the sample revealed that crude glycerol was basic in nature. Therefore, crude glycerol was subjected to a series of treatment steps such as acidification, extraction and adsorption.

Keywords - *Crude Glycerol, impurities, purification, acidification*

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1. INTRODUCTION

The depletion of fossil fuels at a faster rate with the ever growing demands for energy is a big concern in the global energy scenario. The world wide triggered search for alternate energy led to extensive research on biodiesel which has proved to be one of the promising sources of alternative energy in place of fossil fuels. Biodiesel is produced by the transesterification of triglycerides in animal fats or vegetable oils using methanol as solvent and sodium

Departhydroxide or potassium hydroxide as catalyst. During the transesterification process in a biodiesel plant, crude glycerol is obtained as byproduct, which accounts for about 10% (by wt) of the biodiesel produced. Therefore, to scale up the biodiesel plants, conversion of crude glycerol byproduct into value added products is also important for economic sustainability of the biodiesel industries. In general, pure glycerol is used as raw material in the food, pharmaceutical and cosmetic industries. Glycerol, a byproduct from biodiesel plant contains impurities such as methanol, soap, salts, oil and solid organic materials etc along with water and traces of biodiesel. Treatment of crude glycerol is not a feasible option as it is not cost effective. Because of these disadvantages, crude glycerol holds a very less commercial value. It is also not possible to dispose the crude glycerol in environment due to its hazardous nature. It has been reported that the energy content of crude glycerol is 25 MJ/kg when compared to 19.0 MJ/kg for pure glycerol. Therefore crude glycerol can be considered as waste organic material with potential to be used as raw material for production of value added products such as 1,3 – propanediol, ethanol and animal feeds etc and also as raw material for bio energy production. Crude glycerol composition varies based on the feed stock used in biodiesel production and is impure. Therefore pretreatment of crude glycerol is a significant process needed to convert it to a valuable product. The treatment methods employed to treat crude glycerol are filtration, chemical additives, vacuum fractioned distillation, drying, saponification, acidification, neutralization, extraction with polar solvents and adsorption. These methods are basically employed for removal of soaps and free fatty acids by saponification, methanol by extraction, color and odor substances by adsorption, water by distillation and drying.

2. MATERIALS AND METHODOLOGY

2.1 Materials

The crude glycerol used for the study was the byproduct from biodiesel production process. The samples were obtained from biodiesel pilot plant at Gandhi Krishi Vignyana Kendra, University of Agricultural Sciences campus. The chemical used for the characterization and purification studies are of analytical grade.

2.2 Characterization of Crude Glycerol

To determine the treatment method to purify glycerol, its characteristics such as density, alkalinity, ash content and water content were studied. Density of crude glycerol was determined by specific gravity method. Alkalinity test was carried out to determine whether the crude was acidic or basic in nature. The alkalinity of crude glycerol was calculated according to Standard Methods for the Analysis of Oils, Fats and Derivatves, 6th edition, International Union

of Pure and Applied Chemistry. Ash content test was carried out by gravimetric method to determine the amount of total solids present in the crude sample as the presence of the solids are harmful for microbial processes that use glycerol for energy production. Presence of water in the crude glycerol may give rise to unwanted reactions. Water content was determined by simple distillation.

2.3 Purification of Crude Glycerol

Purification of the crude glycerol was carried out to eliminate or lower the concentration of the impurities that can hinder the process of conversion of glycerol to value added products. The purification studies were carried out according to the standard protocol in IUPAC ACD 1980 (6th edition). To identify the method of purification, crude glycerol sample was tested to determine if it was acidic or basic in nature, by an alkaline test. The test showed the crude glycerol was basic in nature and therefore the samples were subjected to acidification. In order to effectively acidify the crude glycerol, experimental trials were carried out by acidifying it with H_2SO_4, HCl and H_3PO_4. A comparative study was carried out to identify the acid that is effective for purification. The acidified samples were later subjected to adsorption to remove color and odorous substances. The final samples were tested to check for their absorbance using UV – VIS Spectrophotometer at a wavelength of 457 nm.

3. RESULTS

3.1 Characterization of Crude Glycerol

Density: Density of crude glycerol was found to be 1083.179kg/m^3

Alkalinity: Alkalinity test by titrimetric method showed that the crude glycerol was alkaline in nature.

Table 1: Alkalinity test data

Trail	V	T	m	Alkalinity
1	1.2	0.1	3.3	3.606
2	1	0.1	3.3	3.102
3	1.1	0.1	3.3	3.394

Where
V = Volume of HCl rundown (ml)
T = Normality of HCl (N)
m = amount of sample taken (g)
Alkalinity = (V* T* 100)/m

The crude glycerol was found to be basic in nature with an alkalinity of 3.367 ml/ g.

Ash Test:
Ash Content of the crude glycerol sample was found to 2.6%.

Water Content: The amount of water present in crude glycerol sample was determined by simple distillation and was found to be 0.33%

2.4 Purification of Crude Glycerol

Crude glycerol was purified by acidifying the sample. Acidification was carried out with HCl, H_2SO_4 and H_3PO_4. The samples acidified with these acids were subjected to extraction with methanol and then to adsorption using activated charcoal, varying the quantity of adsorbent added from 0.2g to 1.0g. The adsorbed samples were then analyzed for absorbance of light at 457nm using UV spectrophotometer to ascertain the removal of color. The results of the adsorption test for samples acidified with HCl, H_2SO_4 and H_3PO_4 are shown in the table below:

Table 2: Absorbance of light at 457nm for samples treated with HCl, H_2SO_4 and H_3PO_4

Sl.No	Charcoal Added, g	Absorbance HCl	H_2SO_4	H_3PO_4
1	0.2	0.201	0.135	0.292
2	0.4	0.203	0.144	0.299
3	0.6	0.231	0.111	0.238
4	0.8	0.170	0.113	0.284
5	1.0	0.172	0.112	0.259

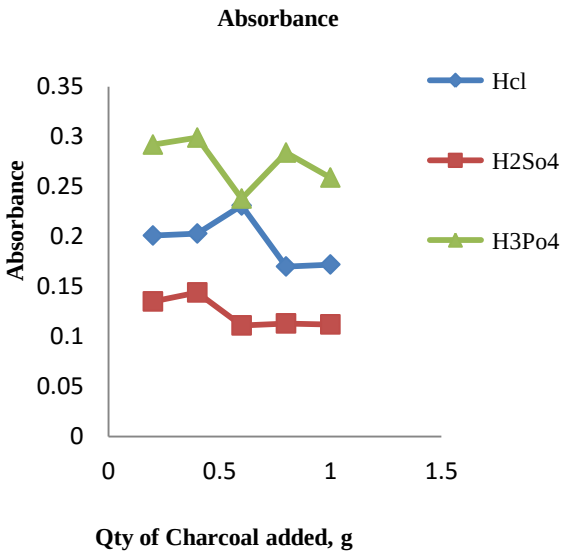

Fig 1: Graph of quantity of charcoal added Vs absorbance for samples treated with HCl, H_2SO_4 and H_3PO_4.

The graph shows that the sample purified with sulphuric acid showed the least absorbance of light at 457nm. Therefore, sulphuric acid was effective in purifying the crude glycerol sample compared to hydrochloric acid or phosphoric acid.

Ash test: The purified samples were subjected to ash test to determine the solids present in it. The ash content of the crude glycerol treated with HCl, H_2SO_4 and H_3PO_4 were tested. It was found that the ash content of the sample treated with H_2SO_4 was lower than the sample treated with the HCl and H_3PO_4. The values are tabulated below.

Table 3: Ash content of the glycerol samples treated with HCl, H_2SO_4 and H_3PO_4

Sl. No	Acidifying Agent	Ash content

1	HCl	0.001
2	H_2SO_4	0.0004
3	H_3PO_4	0.00168

The above data showed that there was 96.1% reduction in ash content in glycerol treated with HCl, 98.4% reduction in glycerol treated with H_2SO_4 and 93.5% reduction in glycerol treated with H_3PO_4. Thus, sulphuric acid proved to be effective in treating the crude glycerol compared to hydrochloric acid and phosphoric acid.

4. CONCLUSION

Glycerol is a byproduct of biodiesel production process and for every ten volume of biodiesel produced nearly one volume of crude glycerol is generated. Thus, there is a very rapid increase of crude glycerol production as the biodiesel production process is being scaled up. The energy content of crude glycerol is considerably high and thus it can be effectively converted to value added products. Crude glycerol is seen as a valuable and cost effective substrate for bioconversion to produce valuable products such as hydrogen, 1,3-propanediol, Phytase, Docosahexaenoic acid, Glyco lipid and animal feed. The impurities present in it limits its application. Hence there is a necessary to purify it before the conversion process.

Acidification could be one of the effective way to purify crude glycerol. The acidification studies showed that treatment with H_2SO_4 can be considered as effective way to purify crude glycerol. Further, studies should be taken up to optimize the strength of the acid needed to increase the purity of the treated glycerol.

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