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Reducing the cost of biodiesel production with support of its by products

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Self-reliance in energy is vital for overall economic development of our country. Biodiesel has attracted considerable attention during the past decade as a renewable, biodegradable and nontoxic fuel. Ttransesterification using alkali as a catalyst is a popular method for biodiesel production. Study explores wastes or byproducts seed cover, de-oiled cake, water wash analysis and its utility for growth of biodiesel industry in future. Study concludes that, it may reduce the cost of biodiesel production and can support biodiesel to commercialize in the form of blending. The reported work is unique, important and interesting.

Keywords: Non-edible oil, biodiesel, transterification, de-oiled cake, brine solution.

Introduction

The stress of diesel fuel is increasing day by day. In future we may face scarcity of fossil fuel. To avoid this problem we should search some renewable energy fuels that may support the fossil fuel as a supplement or substitute for a long period of time and will help to control emissions too. Biodiesel is a bio-product which can be used as a supplement or substitute for diesel fuel (DF). The raw material for biodiesel is essentially oil extracted from plant or animal origin. The oil extracted from plants or animal origin cannot be directly used for diesel engine due to its high density and viscosity[1]. Hence to reduce the density and viscosity of oil, some chemical treatments should be given to the same, that is known as transesterification. The principal role of transesterification is to reduce density and viscosity of oil without reduction in its calorific value[2]. Along with short chain alcohols, homogeneous and heterogeneous catalysts are used in transesterification reaction[3,4]. The synthesized biodiesel will be characterized by ^{1}H NMR spectroscopy. The properties of the biodiesel were determined by American Standards for Testing and Material-6751 (ASTM 6751) and EN 14112. In transesterification, 20% glycerol is obtained as by-product which has high density, viscosity and is semi liquid in nature with a light brown color. It has vast applications as it is used as starting material (feedstock) for soap industry, as well as in pharmaceuticals.

Patil *et al.*[5] have used purified glycerin obtained from transesterification of palm oil using KOH as a base homogenous catalyst and methyl alcohol. It is a major by-product of biodiesel industry and was purified by two methods: adsorption and electrolysis. Glycerin with 80–85% purity has been successfully obtained by electrolysis. The purified glycerol was then characterized by Fourier Transform Infra-Red (FTIR) and High Performance Liquid Chromatography (HPLC). It was reported that waste glycerin was an energy barrier in the process. The raw glycerin were purified by neutralization, microfiltration and ion exchange resins[6]. The purified glycerin was characterized by SEM, XRD and FTIR spectroscopy.

The authors have discussed characteristics of by-products like shelter, de-oiled cake (DOC), biodiesel waste water (BWW) and glycerin in brief. All these products may bring down the overall cost of biodiesel production. India is an agriculture based economy and it supports growing feedstock at the unused agricultural land[7–11]. As the cost of biodiesel production is high as compared to diesel fuel (DF), the authors have focussed the study starting from fruit collection up to the biodiesel production. The obtained co-products may reduce the production cost of biodiesel.

Experimental

Chemicals:

Harvested fresh Jatropha fruits were collected from Indian Biodiesel Corporation Baramati, Maharashtra, India. Chemicals such as sulphuric acid, methyl alcohol, orthophosphoric acid, sodium sulphate were purchased from Merck Ltd. Mumbai, Maharashtra.

Oil extraction:

The fresh fruits contain ~10–12% moisture. So, it was sun dried for 4 days then taken for desheltering process. As the fruits often possess two or three seeds and it often possess a hard outermost shell which bears no oil, it was essential to de-husk the hard and woody part of seeds before carrying out the estimation of oil content. The seeds were separated from shelter or cover by decorticator. The shelter was analysed for determination of calorific value and it was first by-product. The seeds were again dried for 3–4 days in sunlight. Afterward, the seeds were ready for oil extraction and we extracted raw oil by mechanical press extractor. The extractability of oil was examined with at least 10 batches containing 3 kg seed in each batch. For fruit desheltering and oil extraction processes, Jatropha and Pongamia fruits were studied separately. Afterwards, Jatropha seed oil was used for further study. The optimum time required for maximum extractability of oil was 45 min and 55 min for Jatropha and Pongamia seeds respectively. At this stage, we received second by-product that was (DOC), Table 4 shows physical and chemical properties of DOC.

Esterification and transesterification reaction:

Esterification and transesterification reactions were performed in three necked batch reactor of 2 L capacity. First of all 1000 ml Jatropha oil was dehydrated in an oven at 107ºC for 2.5 h. To perform the acid esterification, 100 ml Jatropha oil was used with 1.7% (v/v) sulphuric acid (as a catalyst). The molar ratio of oil and methanol was taken as 1:8. The reaction was performed for 1.0 h at 60±0.5ºC. The speed of mechanical stirrer was kept constant at 600 rpm to overcome limitations due to mass transfer. After completion of reaction, the reaction mixture was transferred to separating funnel for 4 h. Esterified oil was washed with hot water up to 2 times to remove acid content and dehydrated by using rotavapour. Esterified Jatropha oil was used for further transesterification and potassium hydroxide (KOH) was used as a strong base homogeneous catalyst. The optimum reaction conditions were obtained at 1:8 (oil/methanol) molar ratio with 1.0 wt % of potassium hydroxide (KOH) catalyst at 65±0.5ºC for 90 min.The conversion of esters from tryglycerides have been estimated by the eq. (1). The important factors like molar ratio of oil to methanol, catalyst loading, and time of reaction, temperature of reaction and agitation speed were studied separately affecting the yield of methyl ester[3].

$$\text{FAME Conversion\%} = (2A_{ME}/3A\alpha_{CH_2})\times 100 \qquad (1)$$

where A_{ME} shows integration value of protons of methyl ester and $A\alpha_{CH_2}$ indicates integration value of protons on methylene.

After completion and confirmation of reaction, Jatropha methyl ester (JME) was allowed to settle at room temperature for 8 h in a separating funnel. Two distinct layers of raw JME and glycerol were obtained. Due to higher density, glycerol settled at the bottom of separating funnel while methyl ester settled at the top of funnel and it got separated slowly. Both (JME and glycerol) have a substantial amount of the excess methanol that was used in the reaction. It was removed by vacuum distillation. The recovered methyl alcohol can be reused for next batch. Then both the phases were taken for purification. The JME were taken for water wash to remove chemicals like H_2SO_4, and KOH. The small biodiesel batches produced in the lab were washed with hot double distilled water (30ºC) up to 3 times to refine the fuel. The water, 10% v/v (water/biodiesel) was poured gently into a separator funnel used for phase separation. The funnel was gently inverted three times to mix the water through the biodiesel. The water/biodiesel mixture was allowed to settle for 20 min. Sometimes longer settling time was required for the early washes or if high amounts of soap was made. BWW samples were collected in glass mason jars, labelled and stored in the fridge at 4ºC until tested. Afterwards, JME were dried and distilled separately and analyzed. The obtained JME characteristics were shown in Table 1 and that BWW were given in Table 2.

Table 1. Analysis of Jatropha oil and JME

Parameters	ASTM-6751 test method[16]	Jatropha oil[10]	Jatropha methyl ester[4]
Acid value (mg KOH/g)	D664-07	17.88	1.78
Density (g/cc)	D1448-1972	0.940	0.872
Kinematic viscosity (Cst at 40°C)	D664-06	55	4.9
Cloud point	D2500	5	4
Pour point (°C)	D2500	–1	–1
Flash point (°C)	D93	180	167
Fire point (°C)	D93	197	176
Cetane number	D613	51	51
Calorific value	D6751	–	37.5
Water (%)	D2709	7.5%	0.02
Carbon (%)	By elemental analysis	76.11	75.08
Oxygen (%)	By elemental analysis	11.06	11.68
Hydrogen (%)	By elemental analysis	10.52	12.78
Nitrogen (%)	By elemental analysis	0.10	0.09
Sulphur (%)	By elemental analysis	0.013	–

Table 2. Analysis of BWW

Parameters	Unit	BWW 1	BWW2	BWW3	BWW4
pH	–	6.12	6.15	6.40	6.35
Total hardness	mg/L	110	100	101	110
Chloride content	mg/L	30	18	22	19
Oil and grease	mg/L	250	350	150	210
Dissolved solids	mg/L	520	410	482	480
Chemical oxygen demand	mg/L	560	590	510	540
Biological oxygen demand	mg/L	500	300	320	360
Lead (as Pb)	mg/L	Ab	Ab	Ab	Ab
Cadmium (as Cd)	mg/L	Ab	Ab	Ab	Ab
Phosphate	mg/L	0.70	0.6	0.57	0.72
Potassium	mg/L	0.44	0.41	0.3	0.3
Total suspended solids	mg/L	118	110	122	121
Total organic carbon	%	0.43	0.59	–	0.10
Total nitrogen	%	–	–	0.06	0.10

Purification of glycerin:

The separated glycerin was purified with 85% phosphoric acid (H_3PO_4) at 40±4.5ºC. The two distinct layers were formed, one of salt (at the top) and another glycerin (at the bottom). Afterwards, glycerin was separated and neutralized (about pH 6.5–6.7) with sodium hydroxide (NaOH) solution. The glycerol was then heated to remove moisture for 2 h at 100–105ºC. The purified glycerin was stored at room temperature until tested. The analysis of glycerin was shown in Table 3.

Table 3. Analysis of glycerin

Parameters	Values
Colour	Light brown
FFA (%)	0.87
Density (g/cc)	1.19
Viscosity at 28°C	167
Water (%)	0.07

Results and discussion

The shelter or external cover of both the plants does not contain oil. It has fuel application due to its high calorific value. The raw Pongamia shelter is quite hard and has fuel applications directly. It may be used for preparation of wood pellets using binding agents like wheat flour, rice straw, maize etc.

The pH of DOC of Jatropha and Pongamia show that the sample was slightly acidic in nature, as JDOC displayed pH 5.50 while that of PDOC was 5.77. The electrical conductivity (EC) was an important parameter which represents salinity of water sample. High salinity represents the toxicity of specific ion or higher osmatic pressure around the roots of plants that present sufficient absorption of water by roots.

It was found 5.28 dSm^{-1} for Jatropha while that for Pongamia, was 2.77 which it was lower (about 50%) than that of Jatropha. Next major important parameter was percentage of nitrogen in DOC, as nitrogen is major element that is essential for plant growth. Most of the nitrogen (about 80%) is presents in air and plants can absorb it in the form of nitrate or ammonium ion only. JDOC and PDOC contain 6.38% and 5.36% of nitrogen. Phosphorus is an important and major element after nitrogen. JDOC and KDOC contained 1.87% and 0.73% of phosphorus respectively. It is a

Table 4. Analysis of Jatropha and Pongamia DOC

Parameter	Unit	Jatropha DOC	Pongamia DOC
pH (1:5)	–	5.50	5.77
EC (1:5)	dSm^{-1}	5.28	2.77
Moisture	%	7.21	4.14
Organic matter	%	79.05	89.12
Nitrogen	%	6.38	5.36
P_2O_5	%	1.87	0.73
K_2O	%	1.19	0.72
Calcium	%	0.80	0.49
Magnesium	%	0.29	0.18
Sulphur	%	0.29	0.15
Iron	ppm	688	388.5
Manganese	ppm	26.75	19.5
Zinc	ppm	128.40	46.8
Copper	ppm	22.2	17.2
Sodium	%	0.11	0.16
C:N ratio	ppm	7.19:1	9.64:1
Organic carbon	%	45.85	51.69

key element in DNA (deoxyribonucleic acid) and plays important role reproduction and tissue growth. Potassium is next and third major nutrient after nitrogen and phosphorus. It is hygroscopic in nature, therefore it is not available in elemental form. It plays an important role in photosynthesis (CO_2 uptake) and in osmotic regulation (excess water through out by stomata) processes of plant[12], JDOC and KDOC contained 1.19% and 0.72% of potash respectively. The organic carbon was found to be 45.85% and 51.69% in JDOC and PDOC, respectively. Other parameters like calcium, magnesium, sulphur, iron, zinc, manganese, copper, sodium and C:N ratio were also found sufficiently in JDOC and PDOC, respectively. The harmful elements like arsenic, lead, mercury, and nickel were not found in both the samples. All the parameters showed that non edible oil DOC of Jatropha and Pongamia cannot be used as a fodder or food supplement for animal but it may be applicable for organic fertilizers, as the major nutrients like N, P, K and organic carbon content were present in them in acceptable range.

Jatropha raw oil possesses higher density as well as high viscosity. It must be reduced by transesterification reaction. Acid value of crude Jatropha oil was 17.88 mg KOH/g which was lowered to 1.78 mg KOH/g by acid esterification. The different reaction parameters viz. oil to methanol molar ratio, catalyst loading, temperature and reaction time were optimized. The optimum oil and methanol molar ratio was 1:8 with 1.7% (v/v) H_2SO_4 at temperature 60±0.5ºC for 1 h. The optimized parameters for transesterification also showed oil methanol in similar proportion with 0.5 wt% KOH and 90 min time of reaction at 65±0.5ºC. Yield of synthesized biodiesel obtained was 90%. The parameters of the JME like acid value, density, kinematic viscosity, flash point, fire point, cloud point, pour point, cetane number and calorific value were determined following ASTM D6751 standard. Other parameters, such as water (%), carbon (%), oxygen (%), hydrogen (%) and nitrogen (%) were also studied and were within the limit of ASTM standard. Thus, the biodiesel obtained was economically viable and possessed a superior quality.

Analysis of BWW has been shown in Table 2. As pH of all the samples were in acceptable limits, viz. 6.12, 6.15, 6.40 and 6.35, all were near to neutrality range. According to Maharashtra Pollution Control Board (MPCB) and Central Pollution Control Board (CPCB), high alkaline or acidic sewage is not allowed to be discharged in stream or river because it may disturb the aquatic life. The total hardness is an aesthetic quality of water and is caused mostly by the minerals containing calcium and magnesium. But it is measured based on the level of concentration of calcium carbonate. The classification of hardness of water is specified as 0–60 mg/L $CaCO_3$ is soft water, 61–120 mg/L is moderate hard, 120–180 mg/L is hard while ≥181 mg/L is very hard water. Our BWW samples had 110 mg/L, 100 mg/L, 101 mg/L and 110 mg/L $CaCO_3$. So all BWW samples came into moderate hard range of water. Nonreacted triglycerides, trace amount of esters may be available in BWW that is now called as oil and grease, measured in mg/L. Its limit is not given by MPCB or CPCB, but it should not be more than 500 mg/L at 15ºC for 4.5 to 10 pH range. The total dissolved solids (TDS) are of vital importance to the operation of water treatment plants. The TDS range of drinking water is <100 mg/L upto 25000 mg/L, while waste water may contains very high levels of organic compounds. Some of these applications may include water with substantial ionic impurities as well as organic matter. Our BWW samples showed 520 mg/L, 410 mg/L, 482 mg/L and 480 mg/L of TDS which was quite high. Chemical oxygen demand (COD) is a water quality measure used not only to measure the amount of biological active substances such as bacteria but also biologically inactive organic matter in water. It is the oxygen equivalent of the total organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant such as dichromate. BWW samples showed COD as 560 mg/L, 590 mg/L, 510 mg/L, and 540 mg/L. The MPCB and CPCB have not given any limits for COD as well as for BOD of such effluents. But COD is generally higher than BOD for obvious reasons. It is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in water sample at certain temperature over a specific time period. It is used as an indication of the organic quality of water. The lowest BOD quantity is acceptable as it is based on the fact that it is assumed that there will be six times dilution in the river and the river BOD will thus be less than 5 ppm to allow healthy aquatic life. BWW sample contains 500 mg/L, 300 mg/L, 320 mg/L, and 360 mg/L of BOD. Harmful elements like lead and cadmium were not available in BWW. It was therefore less toxic to aquatic life. The role of phosphate and potassium were discussed above. The BWW contains 0.70 mg/L, 0.60 mg/L, 0.57 mg/L, 0.72 mg/L phosphates and 0.44 mg/L, 0.41 mg/L, 0.3 mg/L, 0.3 mg/L potassium were available. The total suspended solids (TSS) can be referred to material which are not dissolved in water and are not filtrate in nature. In short, it is defined as, residue upon evaporation of non filterable sample on a filter paper. The BWW contains 118 mg/L, 110 mg/L, 122 mg/L and 121 mg/L of TSS respectively. TSS exclude light thus reducing the growth of oxygen producing plants. Biologically active suspended solids may include disease causing organisms as well as organisms such as toxic producing strains of algae. The organic nitrogen and carbon did not exceed than 1% respectively.

Glycerin is major and a single by-product of transesterification reaction. Table 3 represents quality parameters of glycerin. It has light brown color and has high density, 1.19 g/cc. Due to its higher density; it gets settled at the bottom of settling tank. Viscosity is directly proportional to density, as density get higher, viscosity is too high, ~167 Cst. That is a reason that glycerin is semi liquid in nature. The extra moisture got reduced upto demoisturization at 105ºC for 2 h. The free fatty acid was 0.87% that was reduced with triglycerides in transesterification reaction.

Economic viability of biodiesel industry:

Economical viability of biodiesel industry is of importance[13,14] and though a detailed cost analysis of the process has not been carried out, our perception says that the work carried out is economically viable. There are four major coproducts obtained in the process, namely fruit shelter, DOC, glycerin and BWW. As biodiesel industry is an agricultural industry and has a focus at least for the last ten years in India. The fruit shelter has good calorific value of 32.174 Mj/kg with a meager mean ash content of 0.04 g/100 g and it may be applied as a fuel directly and has another option to improve its cost is to use it as a feedstock for preparation of fuel pellets. Next co-product is de-oiled cake (DOC) which can be applied as organic fertilizer. Currently fertilizers cost is increasing day by day and poses major hurdle to farmers. So this (DOC) may be low cost solution. BWW is recovered about 3 liters for each liter of methyl ester purification. Huge quantity is produced and it may be applicable as liquid fertilizers (using dilations) and for gardening that will reduce excess use of drinking water. Purified glycerin has most applications in pharmaceuticals and currently used as feedstock by soap industry. Considering above parameters may reduce the cost of biodiesel production and it can be competitive to diesel fuel in economical concern.

Synthesized JME has acceptable physical and chemical properties as per ASTM-6751. Both the feedstocks, Jatropha and Pongamia are easily available throughout the country and both the plants have ability to sustain in extreme conditions. Basic pH range of both DOC were in acceptable limits of neutrality. The presence of nitrogen (6.38% and 5.36%), phosphorus (1.87% and 0.73%) and K (1.19% and 0.72%) which are major nutrients used for plant growth are present in both the materials in significant amount. Some minor elements are also present in the product. Biodiesel waste water (BWW) has pH range near to neutral as per MPCB and CPCB limits. The BWW samples were found moderately hard, oil and grease concentration were in limit but TDS were found slightly high. The COD and BOD represent the quality of water and its limits are not mentioned by MPCB. But compared to other chemical industrial wastes, BWW quality has much good.

Considering all above parameters BWW may be applicable for gardening purpose after necessary pre treatments. And it may be useful as a liquid fertilizer considering present of major nutrients presence in it while harmful elements like lead, cadmium and arsenic were not present. All above parameters may conclude that the BWW could not be allowed to discharge without prior treatments. After treatment, it may be useful for gardening applications as it has acceptable pH, phosphorus, potassium, TSS, organic carbon and nitrogen percentage. The BWW has one more application that it may be used as a liquid organic fertilizer due to presence of phosphate, potassium and nitrogen. The major elements are present in good quantity. Here extra research work with practical trials is necessary. The algal oil for biodiesel synthesis is potential field. It requires potash and nitrogen which grows in short period of time (about a month). We have identified and studied some algal species that are lipid extracting and can grow on our BWW. We have taken positive experimental trials using BWW as a food for algae.

Glycerin is a major and valuable co-product of biodiesel industry obtained about 20% (by weight of oil) in transesterification reaction. Light brown colored glycerin has high density (1.19 g/cc), viscosity (167 Cst) and almost negligible moisture (0.07%). It is used as a feedstock for saponification industry and along with that pure glycerin has vast applications in pharmaceuticals.

Conclusions

The authors have considered the work starting from fruit collection to biodiesel production. We have reported work with the aspect of cost reduction of biodiesel and the results obtained clearly indicate that if all the waste and by-products like fruit shelters, (DOC), glycerol, and (BWW) are meticulously handled, the process will be economically viable. The work is unique, useful and interesting.

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References

1. Dupont, Suraez, M. R. Meneghetti and S. M. P. Menegetti, *Energy & Envi. Sci.*, 2015, **2**, 1258.
2. D. C. Y. C. Leung and Y. Guo, *Fuel Process Technol.*, 2009, **90**, 701.
3. S. B. Chavan, R. R. Kumbhar, Y. C. Sharma, D. Madhu and B. Singh, *RSC Adv.*, 2015, **5**, 63596.
4. R. R. Renish, S. B. Chavan, C. A. Shinde and R. R. Kumbhar, *IREME*, 2015, **9(3)**.
5. P. S. Patil, A. Ghayas, K. Usmani and E. Suryavanshi, *IJSRET*, 2014, **3(6)**, 937.
6. W. R. N. K. Isahak, M. Ismail, M. A. Yarma, J. M. Jahim and J. Salimon, *J. Appl. Sci.*, 2010, **10(21**), 25090.
7. R. R. Kumbhar, S. B. Chavan and V. B. Khyade, *Res. J. Agric. and Forestry Sci.*, 2014, **1(2)**, 12.
8. S. N. Bobade, R. R. Kumbhar and V. B. Khyade, *Res. J. A. F. Sci.*, 2013, **1(2)**, 12.
9. S. B. Penugonda and V. R. Mamilla, *IJEAT*, 2012, **3(1)**, 146.
10. S. B. Chavan, R. R. Kumbhar and R. R. Deshmukh, *RJCS*, 2013, **3(11**), 24.
11. B. Sing, Faizal Bux and Y. C. Sharma, *Chemical Industry and Chem. Engg. Quarterly*, 2011, **17(2**), 117.
12. E. D. B. Silva, E. N. Hizuka., P. H. Grazziotti, D. F. Jose and A. T. Campos, *African J. Agric. R.*, 2015, **10(13)**, 1572.
13. S. B. Chavan, R. R. Kumbhar, A. Kumar and Y. C. Sharma, *ACS Energy Fuels*, 2015, **29**, 4393.
14. S. Merk, *Ecological Chem. and Engg.*, 2011, **18(1**).