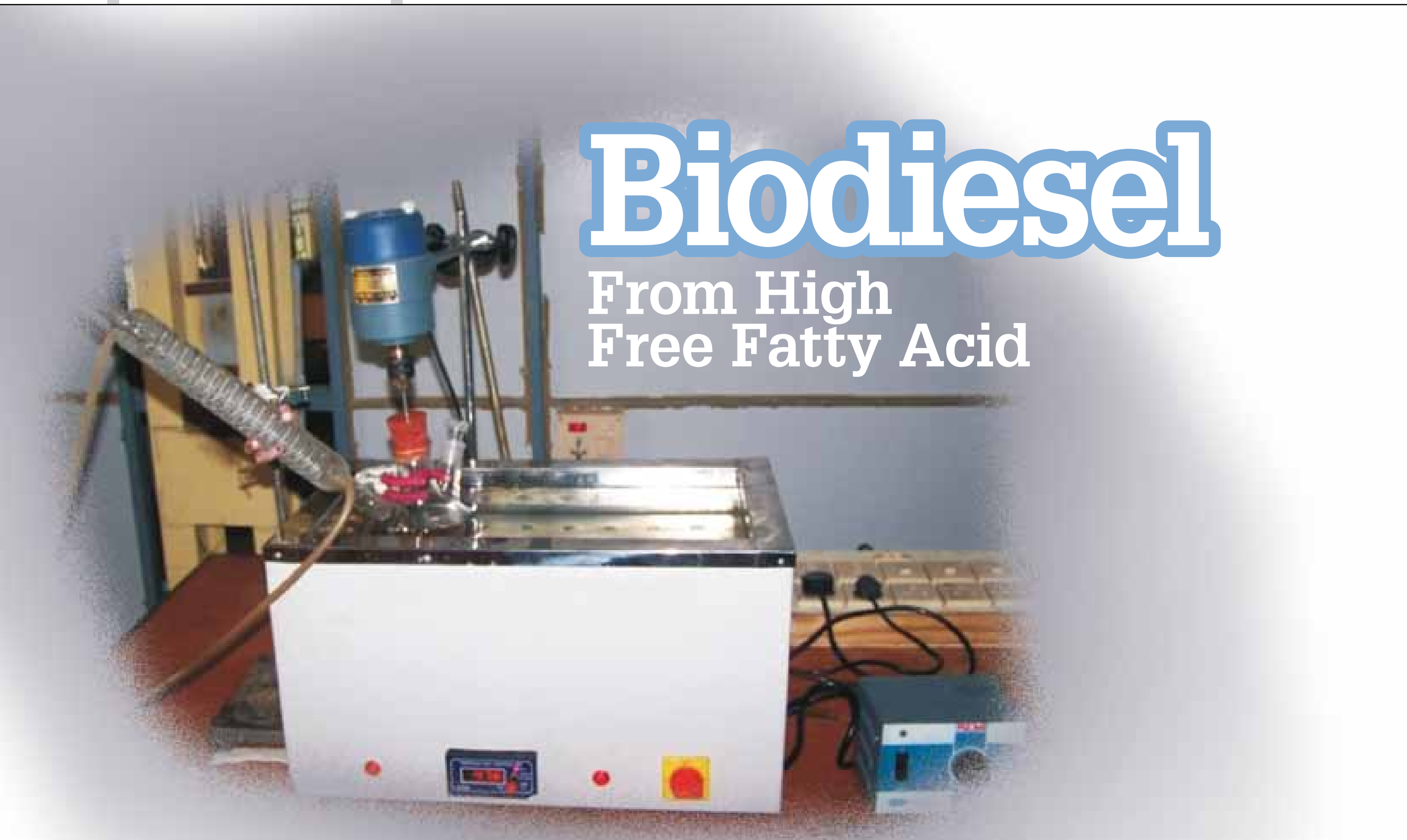
Biodiesel

From High Free Fatty Acid



Pic 1: The transesterification reactor

The Jatropha curcas oil with free fatty acid (FFA) content of 8.81 per cent was subjected to acid pretreatment prior to transesterification during the experiment. The oil was pretreated using sulphuric acid with 25 per cent methanol for 1 hour at 50°C in 200 rpm. The yield of pretreated oil was 95 percent and the FFA content was reduced to 0.65 percent. The pretreated oil was transesterified using 0.5 percent NaOH and 25 per cent methanol for 2 hour at 60°C in 200 rpm. The yield of monoester was 96 percent and the wash water had 17,600 mg/l of COD and 160 mg/l of BOD.

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India is currently the world's fourth largest economy and fifth largest consumer of energy, accounting for 3.7 per cent of world's energy consumption. In recent years, our country's energy consumption has been increasing at a faster rate due to rapid population growth, economic development and increase in the number of vehicles. According to the Ministry of Petroleum and Natural Gas the demands for oil and gas are likely to rise from 180 million tons of oil equivalent in 2008-09 to 233.58 million tons of oil equivalent in 2011-12. With an expected growth rate of oil consumption (14 per cent per annum), shrinking crude oil reserves and limited refining capacity, we have to depend heavily on imports of crude. The high energy demand, dependence on foreign energy sources and wide usage of fossil fuel is leading to a twin crisis namely faster environmental degradation. These factors necessitated a continuous search for an alternative fuel, which promises an agreeable correlation with sustainable development, energy conservation and efficiency and environmental preservation. (Khotoliya et al., 2007).

Most of the alternate fuels namely ethanol, biodiesel, biogas, methanol, etc. are produced from biomass. Among these fuels, biodiesel is identified as a prominent fuel for the transport sector. Biodiesel is a cleaner alternative fuel produced from vegetable oils and fats, through transesterification process using lower alcohols like methanol. For the production of biodiesel, selection of raw material is more important than investment, operating costs and energy consumption.

At present, raw materials for producing biodiesel include refined or semi-refined vegetable oil from soybean, sunflower, rapeseed, palm, peanut, jatropha, pongamia, micro algae, waste cooking oil, waste tallow and other cheap materials (Bao et al., 2008). The oil price contributes to more than 70 to 80 per cent of the total production cost of biodiesel. Most of the countries produce biodiesel from edible oils. In our country, edible oils are in short supply and we need to import 45 per cent of the total requirement. As a remedy to this, the available 100 million hectare of wasteland, conducive climate and cheap work force can be utilized for the production of non edible oil seeds. Based on Clayton (2009), the entire Indian diesel consumption could be replaced by dedicating 45 per cent of these wastelands to plant Jatropha curcas crop. It is one of the drought-resistant shrubs, an oil seed crop, which can be planted to prevent soil erosion, to reclaim land and especially to exclude farm animals. Cultivation of this plant can generate an income of Rs 25,000 per ha in the first year and Rs 1,50,000 from fifth year onwards (Heller, 1996).

The genus Jatropha belongs to *Euphorbiaceae* family and contains approximately 476 species of which 12 are planted in India. Depending on the variety, the decorticated seeds contain 40-60 per cent of oil, which is used for many purposes such as lubricant, for soap making and most importantly for producing biodiesel (Rivera Lorca, 1997).

Materials and Methods

Free fatty acid content of the Jatropha curcas oil was analyzed as per AOCS Ca 5a-40 method. The esterification reaction was carried out in a laboratory scale transesterification reactor.

Pretreatment: A sample of 500 ml of Jatropha curcas oil was allowed to warm up by 50°C. In the acid catalyzed transesterification, sulphuric acid (1 and 2 per cent) was added to methanol (20-25 percent) and the mixture was heated to 50°C for 1 hour. The reacted mixture was transferred to a separating funnel and allowed to separate for 2 hour by gravity.

Transesterification: A sample of 450 ml of acid treated oil was taken for alkali transesterification. The base catalyst (1 - 0.65 per cent) was weighed and dissolved completely in methanol (20-25 per cent) to form sodium methoxide in the base catalyzed transesterification. The acid catalyzed oil was warmed up and the reaction temperature was maintained at 60°C. The sodium methoxide solution was added to the oil and the reaction was carried out for a period of 2 hours and the mixture was transferred to a separating funnel and allowed to settle overnight by gravity. The biodiesel was decanted from the separating funnel and glycerol was drained out.

Water washing of biodiesel: Biodiesel produced from this process contains soap, catalyst and glycerol. While using the biodiesel in engine, deposition of these particles on engine components will occur and the engine parts will be affected. Hence, an equal quantity of ordinary water was taken to remove the contaminants from biodiesel. The washed water was analyzed as per Winkler's method to know the biological oxygen demand (COD) and chemical oxygen demand (COD). The washed water is shown in Pic 2.

> A maximum yield of 96 per cent monoester was reached in the study. Also the effluent generated from the biodiesel wash water had high level of toxicity.

Results and Discussion

FFA content of J.curcas oil: FFA content of J.curcas oil was 8.81 per cent. High FFA in this oil was due to the long storage of oil and seeds. Berchamans (2008) reported similar results, where higher FFA content of the oil was due to the long storage, oxidation and hydrolysis reactions. As reported by Veljkovic (2006) the percentage of FFA and moisture content had significant effect on transesterification of glycerides. The higher FFA content would lead to soap formation and the separation of products would be more difficult, and as a result, yields a lesser biodiesel. Hence, an alternate method such as pretreating the oil with concentrated sulphuric acid was used to reduce the FFA of the oil. The base transesterification was then adopted to produce biodiesel.

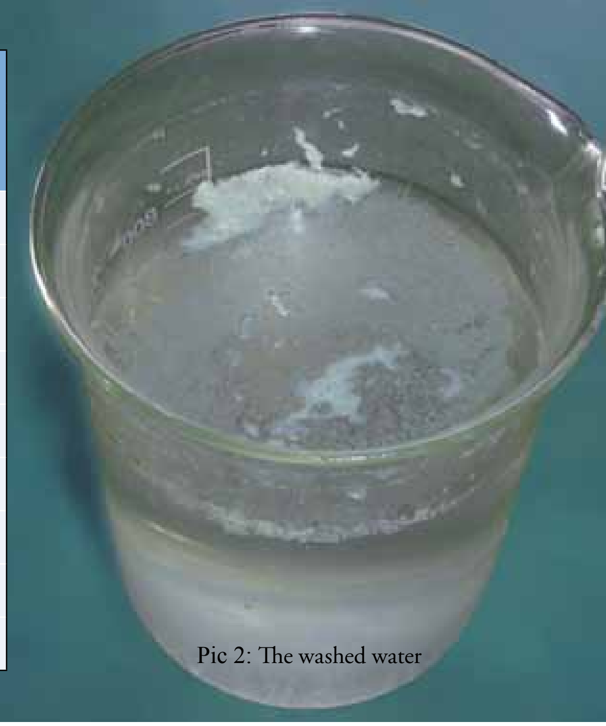
Acid pretreatment: The results of acid pretreatment are presented in Table 1. From this, an increase in the methanol concentration from 20 to 25 percent, promoted the esterification and increased catalyst concentration reduced the FFA content of the oil to a lower level of 0.5 per cent and maximum conversion was achieved at the higher catalyst concentration and higher percentage of methanol, respectively.

Alkaline transesterification: Graph 1 shows the ester yield of the pre-treated oil using alkali treatment. A maximum

Table 1: Acid pretreatment of Jatropha curcas oil

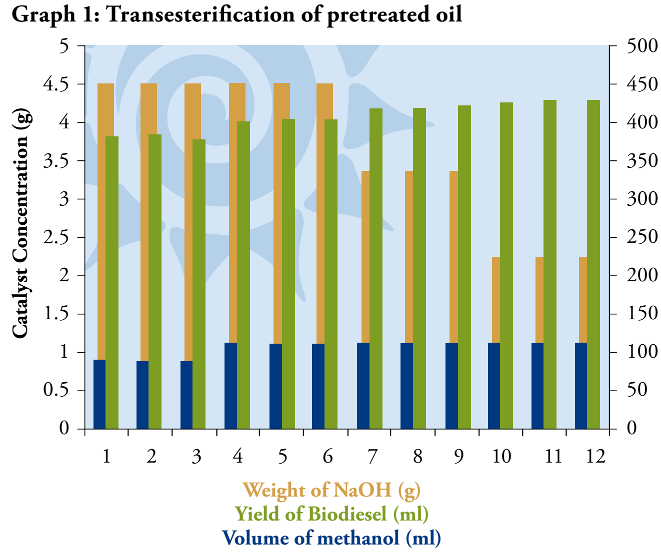
Volume of methanol (ml)	Volume of H_2SO_4 (ml)	Pretreated oil		FFA of the pretreated oil
		Volume (ml)	Percentage of raw oil	
100	5	445	89.0	1.45
100	5	442	88.4	1.60
100	5	447	89.4	1.50
100	10	455	91.0	0.730
100	10	457	91.4	0.770
100	10	460	92.0	0.760
125	10	473	94.6	0.592
125	10	472	94.4	0.603
125	10	474	94.8	0.621

Yield of biodiesel on varied methanol and catalyst concentration



Pic 2: The washed water

Graph 1: Transesterification of pretreated oil



ester yield of 95.8 per cent was obtained at the methanol to oil molar ratio of 7.5:1 and the catalyst concentration of 0.5 per cent. This data revealed that the ester yield increased with increasing methanol concentration from 20 to 25 per cent by reducing catalyst proportion from 1.0 to 0.5 per cent. Increase in the biodiesel production indicates that most of the methanol supplied participated in the reaction. The higher yield of biodiesel at increased methanol proportion may be attributed to the fact that excess quantity of methanol shifts the reaction to ester formation, as transesterification and esterification are reversible reactions (Yun et al. 2008).

Biodiesel effluent: The washed water from biodiesel was analyzed as per Winkler's method. Methanol and glycerol are highly soluble in water hence washing in water is very effective to remove them. However, addition of water for the purification offers a highly polluted liquid effluent that increases the production cost and time. The effluent had 17,600 mg/l of COD and 160 mg/l of BOD. The high concentration of effluent generated from the wash water will act as a pollutant.

Conclusion

The non-edible oils are well suited raw material for biodiesel production. The cost of oil contributes to about 70 per cent of the cost of production of biodiesel. While using the oil with high FFA content or less quality oil, acid catalyst can be used. The present study was carried out using high FFA(8.81 per cent) jatropha oil and a maximum yield of 96 per cent monoester was reached. The effluent generated from the biodiesel wash water had high level of toxicity. Hence, an alternate method to purify or to increase the quality of biodiesel were the recovery of side streams namely methanol and glycerol. It will reduce the production cost of biodiesel and improve its quality. The government has planned to utilize biodiesel with crude diesel in near future; therefore, demand for biodiesel can generate new production systems and employment opportunities with environmental benefits and acceptance.

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