Parametric Studies on Bio-diesel prepared from Rice Bran Oil

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ABSTRACT

Plant oils have quite high viscosity compared to diesel fuel. These can be used as alternate fuel to run a diesel engine but this creates problems of injector coking, dilution of engine oil, deposits in various parts of engine during extended operation of the engine. Esterification of these oils reduces the viscosity to a large extent by converting the oils to bio-diesels. This paper deals with the effect of various parameters on yield and conversion of oil to bio-diesel prepared from rice-bran oil. Molar ratio of 6:1 gave very good conversion and yield of the bio-diesel for reaction time of 4 h but for a reaction time of 6 h, molar ratio of 4:1 was equally good. Percent conversion was almost same at different reaction temperatures. However, percent yield decreased with decrease in reaction temperature. High FFA content in oil affected the bio-diesel yield and the effect was more evident at low reaction temperatures.

Key words: Bio-diesel, reaction time, oil temperature, molar ratio, yield, conversion, rice bran oil

1. INTRODUCTION

Rising petroleum prices, increasing threat to environment from exhaust emissions, global warming and threat of supply instabilities has led to a growing concern for it throughout the world, more so in the petroleum importing countries like India. Petroleum oil reserves are limited but the oil consumption rate is increasing at an alarming rate. For India, petroleum consumption has increased from 18379 thousand tonnes in 1970-71 to 112559 thousand tonnes in 2002-03 (GOI, 2005). Mechanized agriculture food production systems depend heavily on liquid fuels particularly diesel fuel. The role of agriculture as a source of energy resources is gaining in importance (Best, 2006). Therefore, agricultural scientists are more concerned about finding an alternate for diesel fuel. They are interested in biomass-based fuels, as the use of biomass appears to be a viable alternative, especially for the on-farm use of fuels in tractors, combines, and stationary diesel engines. Some of the biomass-based fuels, which have been tried as a partial or complete substitute fuel in the IC engines, include alcohols (Bandel, 1977), biogas (Dass *et al.*, 1978) and vegetable oils (Shyam, 1984). Amongst these, plant oils are considered very good alternate fuel for diesel engines. These offer several advantages over other alternate fuels.

It has been reported that in diesel engines, crude plant oils can be used as fuel, straight as well as in blend with the diesel (Shyam, 1984). However, during extended operation of the engine, problems of injector coking, dilution of engine oil, deposits in various parts of engine, etc. have

been reported. The major drawback with the vegetable oils as fuels is their high viscosity (Ryan *et al.*, 1982). Esterification is one method to reduce viscosity of plant oils. It gives plant oil bio-diesels commonly known as bio-diesels. Several researchers (Verma *et al.*, 1998, Krahl *et al*, 2005, and Gupta, 1994) used bio-diesel as alternate fuel in the existing CI engines without any modification. Promising results have been obtained in running of CI engines on plant oil based bio-diesels. Studies have also been conducted on the long term running of CI engines using these fuels.

In bio-diesel production process, the main variables that affect the bio-diesel yield and percent conversion of oil to bio-diesel are alcohol to oil molar-ratio, type of alcohol used, type and amount of catalyst used, reaction time, mixing temperature, and reaction temperature. This paper deals with the effect of such parameters in case of bio-diesel from Rice bran oil.

2. MATERIALS AND METHODS

Physically refined rice bran oil was purchased from a mill located in Punjab (India). Bio-diesel was produced in the laboratory using the simple method standardized by Gupta (1994). The catalyst used (NaOH pellets) was of SQ grade with 97% purity while the methanol used was of LR grade with 99% purity. The method is explained in the process flow diagram, Figure 1. Each time, oil sample of 30 ml was taken for conversion to its methyl ester i.e. bio-diesel. The volume of dried bio-diesel was noted to calculate per cent bio-diesel yield.

2.1 Fuel Characteristics of Rice Bran Oil

Fuel characteristics of rice bran oil used for the study were determined and are given in Table 1.

Table 1. Fuel characteristics of rice bran oil

Density at 21ºC, g/ml	Viscosity at 38ºC, cS	Cloud point, ºC	Pour point, ºC	Flash point, ºC	Gross heat value, MJ/kg	Free fatty acid, percent
0.923	42.2	11	-1	258	42.3	0.15

2.2 Estimation of Conversion of Oil to Bio-diesel

Percentage of oil converted to bio-diesel was measured by the modified method of Sangha *et al.* (2000). For estimating the exact amount of per cent conversion, a spectrophotometric method was developed and standardized. This method basically involved the estimation of glycerides present in the form of unconverted oil in the prepared ester. Total glycerides in the oil and unconverted was done in terms of glycerol, which was obtained after saponification of the test sample.

Saponification was done by the method suggested by Sastry and Kates, as reported by Work and Work (4). Two ml sample of oil/ester was taken in a round-bottomed flask. Then 0.8 ml of 33% aqueous potassium hydroxide and 20 ml of 95% ethyl alcohol were added to it. This mixture was refluxed for 90 minutes on boiling water bath. Immediately after refluxing, 20 ml of 2N HC1

was added. Thereafter, the mixture was cooled and 40 ml of petroleum ether (40°C - 60°C) was added. The solution was thoroughly mixed again and allowed to settle down for about 20 minutes. The upper layer of the petroleum ether containing FFA was discarded. The lower layer of the ethanol water containing the glycerol was evaporated to half the volume in order to remove the excess alcohol. Then, the volume of the solution containing glycerol was doubled with distilled water. Glycerol in the above solution was estimated by the method of Renkonen as reported by Work and Work (4). Glycerol estimation directly gave the total glyceride content in the solution. In this method, 0.5 ml of the sample was taken. Then 0.5 ml of distilled water & 0.1 ml of 10N H_2SO_4 was added to it followed by addition of 0.5 ml of 0.1M sodium periodate ($NaIO_4$). It was mixed thoroughly and left at room temperature for 5 minutes. Thereafter, 0.5 ml of 10% sodium bisulfite ($NaHSO_3$) was added to it followed by addition of 5 ml of chromotropic acid reagent (0.18%, 100 mg dissolved in 10 ml distilled water & added to it 45 ml of 24N H_2SO_4), which was the final colouring agent. The contents were mixed thoroughly and the tubes were placed in boiling water bath for approximately 2 hrs. The tubes were cooled and the absorbance of solution was recorded at 570 nm. Standard glycerol (0.02 micromole –0.1 micromole) and a blank containing distilled water was also run simultaneously. The final colouring agent, chromotropic acid had to be added with utmost care, as even a single drop of it could cause variations in the reading. Thus, the absolute reading of the sample could vary from time to time, but the per cent conversion was always the same with S.D. of ± 3.

Amount of glycerides was calculated in terms of micromoles of glycerol (glyceride) per ml of sample. Total glyceride in the oil and the unconverted glyceride present in the ester were determined. Finally, the percentage of ester formed from oil was calculated by subtracting unconverted glyceride from the total glycerides.

2.3 Parameters Studied

The independent parameters studied were methanol to oil molar ratio, oil temperature, oil moisture, and extremely low ambient temperature. Methanol to oil molar ratio was varied from 4:1 to 6:1, oil temperature from 30°C to 60°C, reaction temperature from 20°C to 40°C, amount of free fatty acid from 0.6% to 3.0%, and extremely low ambient temperature from 4°C –9°C. Percent oil to bio-diesel conversion and percent bio-diesel yield were taken as the dependent parameters.

In the bio-diesel production process, after mixing alkaline methanol with oil, the mixture was kept undisturbed for 4 to 6 hours. Immediately after mixing, the temperature of the mixture dropped from 60ºC to 40± 2ºC and slowly became equal to the ambient temperature. The ambient temperature varied with the season and, as such, affected glycerol separation from the reaction mixture. Therefore, the effect of reaction temperature was also studied. Experiments were conducted in which the alkaline-methanol were mixed with rice bran oil at 60ºC (molar ratio 6:1) and the mixture was then maintained at different temperatures (reaction temperatures) of 20, 30, and 40ºC in an incubator to study the effect of reaction temperature.

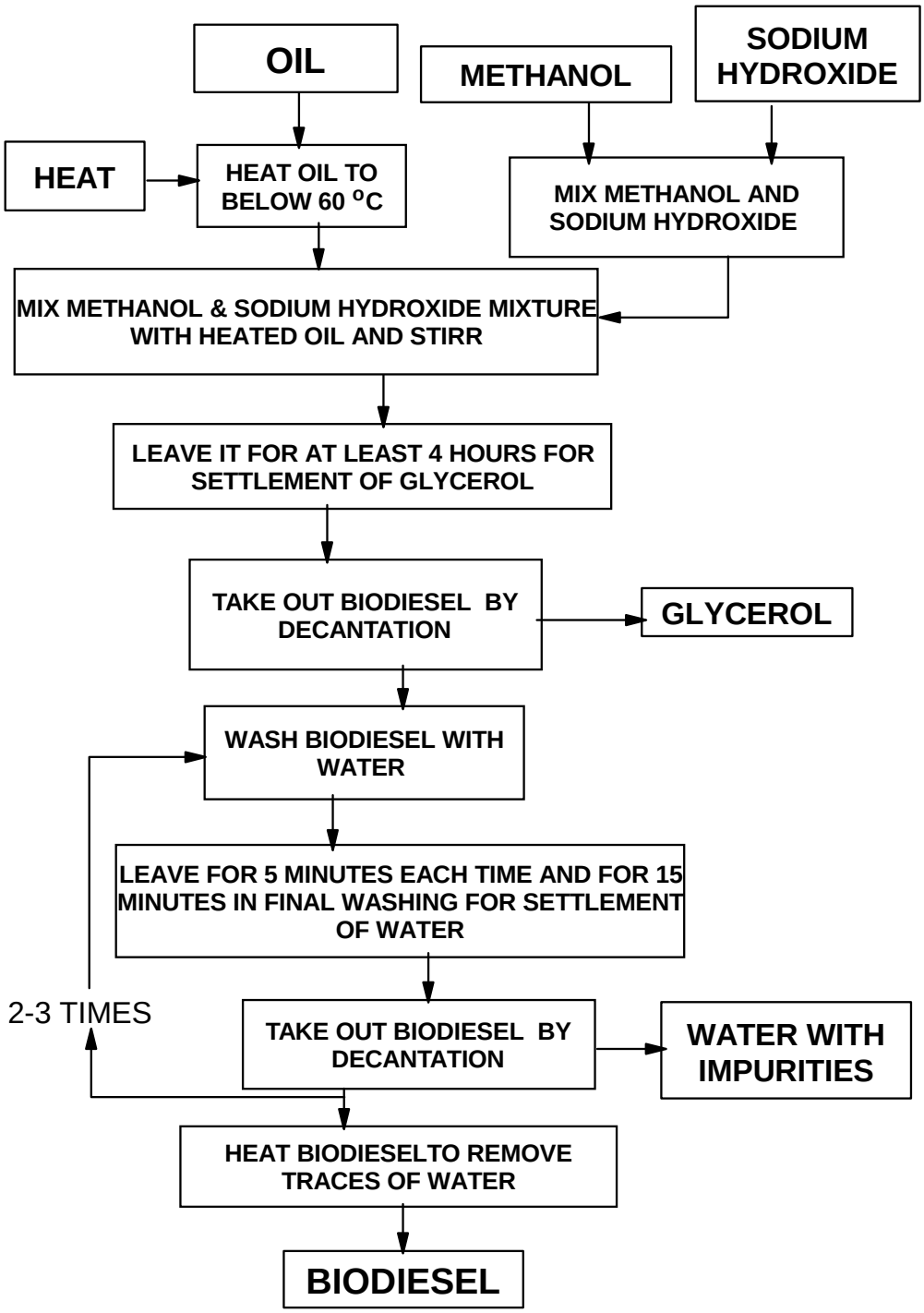

Figure 1. Process flow diagram for production of bio-diesel

Effect of different concentrations of oil FFA on conversion and yield of bio-diesel was also studied. The FFA content in physically refined rice bran oil was found to be 0.61%. Amounts of FFA to be added to the refined oil, for preparing samples of rice bran oil having different FFA concentrations, were calculated. Slightly higher amounts of FFA (20-40 mg) than the calculated ones were added because the FFA obtained from the mill was not 100% pure. After mixing the said FFA in the oil, the FFA content of the oil samples was actually measured.

3. RESULTS AND DISCUSSION

Different experiments were conducted at different times in a year. Therefore, some conditions (e.g. ambient temperature etc.) might not be exactly same for all the experiments. As such, the results of different sets for studying a particular parameter are independent and not comparable with the results of other set.

3.1 Effect of Molar Ratio

Studies were conducted to determine the affect of molar ratios. Three methanol to oil molar ratios of 4:1, 5:1, and 6:1 were used for the study. At each molar ratio, seven reaction times (15, 30, 45, 60, 120, 240, and 360 minutes) were studied. As such, at each molar ratio, fourteen samples (of 30-ml oil each) were studied. Each set of tests took about 4-5 complete working days. The results are shown in Table 2.

Table 2. Effect of reaction time and methanol to oil molar ratio

Serial No.	Reaction Time, min.	Percent conversion at molar ratio			Percent yield at molar ratio		
		4:1	5:1	6:1	4:1	5:1	6:1
1	15	85	89	93	45	46	62
2	30	86	89	94	53	54	66
3	45	88	91	94	57	59	72
4	60	90	92	94	61	67	77
5	120	91	93	94	66	67	72
6	240	92	94	95	66	67	82
7	360	92	95	97	83	82	83

It is clear from the Table 2 that percent conversion increased with increase in molar ratio as well as with increase in reaction time. Percent conversion as high as 97% was achieved at molar ratio of 6:1 and reaction time of 6 h. Percent conversion was more than 90% just after one hour even at a molar ratio of 4:1. Hawkins and Fuls (1982) suggested that the bio-diesel yield should be at least 90% for its use in diesel engines. Percent yield also increased with increase in molar ratio as well as reaction time. However, after 6 h, the yield was almost same with the three molar ratios.

At molar ratios of 4 and 5, there was significant increase in yield when the reaction time was increased from 4 to 6 h. However, conversion did not differ much for all the molar ratios as the time was increased from 4 to 6 hours.

Among the three molar ratios studied, ratio 6:1 gave the best results. Hence, ratios 5.5:1 and 6.5:1 were also studied at the same reaction times as considered for molar ratios 4, 5, and 6 to obtain the optimum conditions for maximum conversion and yield of bio-diesel from rice bran oil (Table 3). It is clear from Table 3 that at both the molar ratios i.e. 5.5 and 6.5, the conversion was above 90% and it was almost same at all the reaction times for these ratios. Molar ratio of 6.5 resulted in reduced bio-diesel yield. Perhaps too excess methanol interferes with glycerol separation.

The molar ratio of 6:1 gave very good conversion and yield of the bio-diesel for reaction time of 4 h but for a reaction time of 6 h, molar ratio of 4:1 was found to be equally good.

Table 3. Effect of reaction time and methanol to oil molar ratio

Serial No.	Reaction time, min.	Percent conversion at molar ratio		Percent yield at molar ratio	
		5.5:1	6.5:1	5.5:1	6.5:1
1.	15	94	95	48	45
2.	30	96	96	54	49
3.	60	97	97	52	48
4	120	96	97	58	54
5.	240	96	96	72	62
6.	360	95	97	79	70

3.2 Effect of Oil Temperature

In bio-diesel preparation process used, the oil is normally heated up to 60°C. Studies were conducted at lower oil temperatures also. This was done to determine the effect of heating of oil on the bio-diesel conversion and yield.

Bio-diesel preparation procedures remained the same except that the temperature, to which the oil was heated, was varied. Temperatures of 30, 40, and 50°C were used in addition to the normally used 60°C. At first, the tests were conducted for 40, 50, and 60°C at seven reaction times (15, 30, 60, 120, 240, 360 and 1440 minutes). Later on tests were also done for 30°C but only for 4, 6, and 24 h reaction time. The results are given in Table 4.

The conversion was almost same (>95%) at all the temperatures for reaction time of 4, 6, and 24 h. The yield follows an increasing trend with increase in oil temperature. This may be attributed to the fact that a higher initial temperature helps in faster settlement of glycerol. It was also

observed that allowing the settlement of glycerol for long hours (24 h) did not increase bio-diesel yield. Besides, the percentage of oil converted to bio-diesel in all cases attained the equilibrium value of 95%.

Table 4. Effect of oil temperature (methanol to oil ratio=6:1)

Reaction Time, min	percent conversion at				percent yield at			
	30ºC	40ºC	50ºC	60ºC	30ºC	40ºC	50ºC	60ºC
15	-	94	98	94	-	52	57	59
30	-	96	98	94	-	53	60	64
60	-	95	97	95	-	53	64	66
120	-	96	95	96	-	60	64	66
240	97	97	97	96	63	69	70	74
360	97	97	97	97	70	70	70	81
1440	95	96	95	96	73	70	74	81

Since the percentage conversion after 4 hours was nearly the same for all the temperatures studied, effect of a little lower molar ratio only on the bio-diesel yield was studied. The results are given in Table 5. It is clear from the table that there was no significant change in the yield when the molar ratio was decreased from 6 to 5.5. This was true for both the reaction times of 4 and 6 h. Further studies are, therefore, needed for different molar ratios (may be 5 to 7) with longer reaction time (may be 24 h) to study the bio-diesel yield.

Table 5. Effect of oil temperature

Oil temperature, Degree Celsius	Percent bio-diesel yield			
	After 4 hours at molar ratio		After 6 hours at molar ratio	
	5.5:1	6:1	5.5:1	6:1
30	68	68	68	68
40	68	73	70	70
50	70	71	70	70
60	71	72	75	76

3.3 Effect of Reaction Temperature

As discussed above, reaction temperatures of 20, 30, and 40ºC were studied. Percent conversion and yield were measured after 2, 4, and 6 h and results are given in Table 6.

Table 6. Effect of ambient temperature (molar ratio 6:1)

Reaction Time, h	Percent conversion at			Percent yield at		
	20ºC	30ºC	40ºC	20ºC	30ºC	40ºC
2	95	95	96	48	57	67
4	96	96	96	53	57	67
6	96	96	96	58	65	73

It is obvious from the table that percent conversion was almost same at different reaction temperatures and reaction times. However, percent yield went down with decrease in reaction temperature. It may be due to problems in glycerol separation. This suggests that further studies should be conducted at different molar ratios for determining the possibility of getting better bio-diesel yield even at low reaction temperatures i.e. during cold weather.

3.4 Effect of Free Fatty Acid (FFA) Content in the Oil

Bio-diesel was prepared from the oil samples prepared with known amount of FFA as discussed above. The sample was kept at 30ºC for 6 h duration. Initially the tests were conducted only up to 3.0% FFA content in steps of 0.5%. Percent conversion and yield of bio-diesel was determined as given in Table 7.

Table 7. Effect of oil FFA content at reaction temperature of 30ºC

Required FFA, %	Calculated FFA to be added in 100 ml oil, mg	Measured FFA, %	Percent Conversion	Percent Yield
0.6	Nil	0.61	99	80
1.0	390	0.92	99	78
1.5	890	1.53	99	78
2.0	1390	1.99	99	76
2.5	1890	2.76	99	75
3.0	2390	3.06	96	76

(molar ratio 6:1, reaction time 6 h)

It is clear from the Table 7 that higher FFA content in the oil did not affect the percent conversion appreciably but the bio-diesel yield decreased with increase in FFA. This may be due to loss of oil in saponification. Further tests were conducted to include higher FFA contents up to

8% and at lower reaction temperature (i.e. room temperature of about 12ºC). The results are given in Table 8.

Table 8 shows that the percent conversion as well as the yield decreased with increase in FFA. At room temperature (12°C), FFA contents of more than 5.0% resulted in very low yield and conversion. Even at 30ºC reaction temperature, more than 6.0% FFA affected conversion and yield significantly.

Table 8. Effect of oil FFA content at different reaction temperatures

Required FFA, %	Calculated FFA to be added in 100 ml oil, mg	Measured FFA after-wards, %	% Conversion at reaction temperatures		% Yield at reaction temperatures	
			12°C (room temp.)	30ºC	12°C (Room temp.)	30ºC
3.5	2890	3.37	95	96	78	82
4.0	3390	3.98	94	96	76	82
5.0	4390	5.21	93	94	74	76
6.0	5390	6.44	90	93	64	70
8.0	7390	8.80	-	83	-	66

(molar ratio 6:1, reaction time 6 h)

The following observations were also made:

i) High FFA interference became apparent at FFA content of 6.0% and above. At high FFA content, when alkaline methanol was mixed with oil, it showed gel-like appearance.
ii) Glycerol separation was not proper at room temperature (12°C) for oil samples having FFA more than 6.0%. As such, it was not possible to measure the conversion and the yield. But this problem was not faced at 30°C.
iii) At higher FFA, washing water temperature affected the bio-diesel yield. Washings given with warm water facilitated better yield.
iv) The interference of high FFA content was more evident at low temperatures. Hence, during the winter months, better results are expected if the process is allowed to proceed at relatively higher temperatures.

3.5 Effect of Oil Moisture

During winters, rice bran oil showed some wax settlements. As such, only the oil in the upper portion was clear and transparent while in the lower portion, the oil was turbid and slightly more viscous. The TLC plates of oil from the two portions were identical, but on heating, oil from the lower portion showed some traces of moisture. Therefore, formation of gel during bio-diesel preparation might be due to the presence of moisture as well as because of low temperatures,

which hindered glycerol separation. Hence, the oil from the two portions was separately tried for bio-diesel production and results are given in Table 9.

Table 9. Bio-diesel prepared from clear and settled oil

Variables			Percent conversion with		Percent yield with	
Oil heated/ Not heated	Reaction temperature, °C	Reaction time, hr	Clear oil	Settled oil	Clear oil	Settled oil
Heated*	12°C**	4	92	89	77	64
Heated	30	4	96	96	84	78
Not heated	30	4	95	91	78	70
Heated	30	24	92	90	84	80

* Oil was heated to 100°C to remove traces of moisture, if present

** Room temperature

It is obvious from Table 9 that oil from settled region resulted in lesser bio-diesel yield as well as lesser percent conversion. The effect was more evident for percent yield compared to that for percent conversion. The effect was also more pronounced at room temperature (<12°C) compared to that at reaction temperature of 30°C. Heating the oil to 100°C (to remove traces of moisture, if any), helped in better percent conversion and yield.

It was also observed that bio-diesel from the settled oil became very viscous in a short time when kept at room temperature (<12°C) whereas the bio-diesel from clear oil showed a thin white crystalline layer settlement at the bottom with clear and transparent bio-diesel above it.

3.6 Effect of Extremely Low Ambient Temperature

During extremely cold weather, when the ambient temperature was around 9ºC during the day and dipped to 4-5ºC at night, some problems were faced during bio-diesel preparation from rice bran oil at room temperature. The following observations were made.

In case the process was carried out at room temperature (after heating oil to 60ºC), the volume of unwashed bio-diesel yield was less than that obtained otherwise. Washings given with warm water gave better bio-diesel yield than washings given with tap water.

When the bio-diesel (in unwashed form or still not separated from glycerol) was passed through cold conditions (i.e. when kept overnight during cold weather), glycerol separation was not clearly marked and formation of a gel was observed. However, bio-diesel was obtained when this gel was washed with hot water. The bio-diesel so produced, remained clear even when it was passed through cold conditions. If the gel was heated before washing, bio-diesel yield was not satisfactory.

When the washed bio-diesel was kept at low temperature in a normal plastic container (2 l size) for long periods (overnight), a thin transparent layer settled at the bottom, may be due to settlement of wax. However, when the clear bio-diesel was decanted from top, it remained clear with no settlements later on.

4. CONCLUSIONS

Per cent conversion as well as yield was good at molar ratio of 6:1, reaction time of 4 hour and oil temperature of 60^{o}C. Yield showed an increasing trend with increase in oil temperature or reaction temperature. However, oil temperature and reaction temperature did not affect the per cent conversion much. Increase in FFA content resulted in decreased yield but conversion remained unaffected. Washing of bio-diesel with warm water prepared from oil of high FFA facilitates better yield. Heating of oil to 100^{o}C (to remove traces of moisture) helps in better conversion and yield of bio-diesel. Bio-diesel prepared under low ambient temperature should be given washing with warm water in order to obtain good yield.

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