Nat. Volatiles & Essent. Oils, 2021; 8(4): 16614-16623

Studies On Biodiesel: A Plant-Oil Based Renewable Fuel

Kushagra Mall[1] , Mohd. Abid[2] , Prabhakar Verma[3] , Sonu Daryani[4] And Tej Pratap Singh[5*]

[1,2,3,4]department Of Chemical Engineering, Bundelkhand Institute Of Engineering And Technology, Kanpur Road Jhansi-284128, Uttar Pradesh, India.

[5*]Assistant Professor, Department Of Chemical Engineering, Bundelkhand Institute Of Engineering And Technology, Kanpur Road Jhansi-284128, Uttar Pradesh, India.

ABSTRACT

In this present study, we see that developing countries are looking toward bio-fuel as an energy substitute for fossil fuels and biodiesel is one of the most promising biofuels that can fulfil our energy needs in future. Biodiesel is produced from oil carrying plants and this paper investigates the production of biodiesel from mustard oil seeds and sunflower oil seeds. Mustard biodiesel & sunflower biodiesel is obtained from mustard oil seeds and sunflower oil seeds get their energy from the bond found in fatty acid and methyl ester. The oils are found in mustard seeds & sunflower seeds can be converted into a superior quality diesel fuel. The quality of biodiesel produced is analyzed by its properties like flash point, fire point, density, octane number, cetane number, pour point, acid value, saponification value, iodine value, kinematic viscosity, calorific value. This paper investigates the production of mustard & sunflower biodiesel and compares the properties of mustard & sunflower biodiesel with conventional biodiesel, so that mustard biodiesel can be used in standard diesel engines without modification.

KEYWORDS Bio-diesel, Fatty Acid, Methyl Esters, Trans-esterification Reaction,

1. INTRODUCTION

Energy is the first and foremost requirement for conducting all kinds of activities by human beings. Everything happening around the world is the expression and manifestation of the flow of energy in one or the other forms. Energy consumption can easily be considered an index of development and energy be considered an important input for all sectors of a country's economic development. The last decade of the 20th century has witnessed many discussions on energy throughout the world and some increasingly important new policies, technologies, economic, and political attitudes. Although the changes have been small and to date have not had much impact that many of us wish they would have, they signal the coming of a new revolution. The world as we have known is changing dramatically. The past few decades, which were characterized by abundant supplies of cheap energy, are no longer with us. In the future, energy will be more costly and less available and at the same time in greater demand due to a growing world population and growing aspirations of its population. To avoid world conflicts and economic disruptions as cheap fossil fuels become scarcer and their mal-distribution becomes more acute, new perspectives are required leading to long-term planning within nations and between them. A new area is emerging in which there exist opportunities and challenges in social, political, and economic terms for interdependence and partnership between the developed and developing countries so p that the imbalance in resource utilization by the world countries is avoided and it is more evenly balanced. Fortunately, we are also at a time when there is a growing awareness of the importance and vital necessity of energy. It is being developed to help increase the efficiency with which we ere are many economic, social and technical measures to understand the importance of energy and accordingly use our precious energy resources. It is hoped that with energy conservation programs being made as people's programs and increased use of renewable sources, the energy situation will be easier & better.

Table 1.1: Per cent use of various sources for the total energy consumption in the world

Serial Number	Sources of Energy	Consumption (%)
1.	Coal	32.50
2.	Oil	38.30
3.	Gas	19.00
4.	Uranium	0.13
5.	Hydro	2.00
6.	Wood	6.60
7.	Dung	1.20
8.	Waste	0.30

1.1NATIONAL AND GLOBAL ENERGY SCENARIO

The energy consumption in India has over the years grown at 6-7 per cent per annum against a world average of 1.5 per cent per annum. In India's share of energy consumption, oil and gas play a key role and account for 54 per cent of India's commercial energy consumption. India is the eighth-largest consumer of oil in the world. The energy demand is driven by vibrant economic growth.

Chandra A. (C-1) has reported that the average per capita consumption of a petroleum product in India is 113 kg against a world average of 927 kg. The petroleum product consumption in India is expected to grow from the present level of 97 million tonnes per annum (MTPa) in 1999-2000 to about 180 (MTPa) in 2006-07 and further to around 370 (MTPa) by 2024-25. Similarly, the demand for natural gas which was 110 million standard cubic meters per day (mcmd) in 1999-2000, is expected 231 mcmd by 2006-07 and further to 391 mcmd by 2024-25. Against such high demand projection, the current domestic production of crude oil is around 32 million tonnes a year and that of natural gas around 78 mcmd.

Rai G. D. (R-1) has compared the annual per capita income of various countries and per head energy consumption and has reported that the per capita energy consumption is a measure of the prosperity of the nation. The per capita income of the USA is about 50 times more than the per capita income of India, and so also is the per capita energy consumption. The per capita energy consumption in the USA is 8000 kWh per year, whereas the per capita energy consumption in India is 150 kWh. The USA with 7% of the world's population consumes 32% of the total energy consumed in the world, whereas India, a developing country with 20% of the world's population consumes only 1% of the total energy consumed in the world. Therefore, one might conclude that to be materially prosperous, a human being needs to consume more and more energy than his own. The percentage use of various sources for the total energy consumption in the world is given in Table 1.1. It is apparent from Table 1.1 that the world's energy supplies come mainly from fossil fuels. One of the most significant aspects of the current energy consumption pattern in many developing countries is that non-commercial sources such as firewood, animal dung and agricultural waste represent a significant 8% of the total energy used in the world. This constitutes about 4 times the energy produced by hydro and 60 times the energy produced by nuclear sources. In some developing countries, non-commercial energy sources are a significant fraction of the total resources. This dependence of the developing countries is likely to continue unless replaced by another alternative source of energy.

It is well fact that the known sources of fossil fuels in the world are depleting very fast, resulting in an uncertain supply of energy and/or rising energy costs which in turn will create a crisis of energy. This crisis of energy may be due to two reasons; firstly, the population of the world has increased rapidly and secondly the standard of living of human beings has increased. Anon (A-1) has reported that one-fourth of the world population is facing a crisis of energy and are bound to live without power. On the issue of the constant development of the world, a report revealed the fact that about 25% of the total world population is living without electricity. This stunning truth came out at the "Earth conference" held in Johannesburg, South Africa.

"International Energy Agency", Paris has released a report saying that 160 million people all over the world are deprived of electricity. In its report, it is quoted that 240 million people in the world are dependent on traditional sources for cooking food and generating heat. This source is generally wood and this number would go up to 260 million by 2030. According to the report, in the villages of developing nations such as in South Asia and Africa, every four out of five people are living without power. If such a situation of energy scarcity continues then this number is expected to grow up to 140 million. The report further said that investment in various fields of energy has, become an important need for the present, otherwise, it will create a serious situation leading to massive energy shortages that will be tantamount to an energy crisis. It also emphasized the use of more renewable energy resources. The population of India is also increasing at the rate of about 2.1% per annum which at present has crossed the 100 crore mark. The population of India is also increasing at the rate of about 2.1% per annum which at present has crossed the 100 crore mark. Therefore, the need for energy for a most populous and developing country like ours is paramount and it warrants significant efforts to meet our future energy needs: domestic, institutional, commercial, agricultural and industrial requirements with higher satisfaction of achieving our goals set in the energy sector.

the organic matter directly into premium fuels by a wet process like anaerobic digestion or fermentation. Most importantly, refined biofuels can be utilized in existing fuels systems, often with little or no modification, and are compatible with current patterns of energy use. This improves their economic potential and the speed with which they can be introduced. Refined biofuels have high calorific values.

Sr. No.	Conversion Process	Solids	Principles Products Liquid	Gases	Further Treatment	Premium Fuels
1.	Oil Extraction	-	Vegetable Oil	-	Esterification	Diesel substitute
2.	Chemical Reduction	-	Mixture of oils	-	Fractional Distillation	Hydrocarbon on liquids
3.	Thermal Processes Hydrogenation	-	Mixture of oils	-	Fractional Distillation	Hydrocarbon on liquids
4.	Wet Process Anaerobic Digestion	-	-	Methane and Carbon dioxide	Carbon dioxide removal	Methane
5.	Fermentation	-	Ethanol	-	Distillation	Ethanol
6.	Thermal Process: a) Liquefication b) Gasification c) Steam Gasification	 Char Char Char	Pyroligneous Acids oils and tars	Fuel gas[b] Fuel gas[a,c] Methane[c]	Steam reforming and/or shift reaction	Methane Ethanol or Higher Alcohols

Table 1.2: Premium fuels from biomass conversions

Note: a. Low Calorific Value (5-10 MJ/m^3)
b. Medium Calorific Value (10-25 MJ/m^3)
c. High Calorific Value (30-45 MJ/m^3)

Source: Rai G.D. (1997)
Non-Conventional Energy Sources
Khanna Publishers, Delhi

1.2 BIODIESEL

Vegetable oil and alcohols are now replacing petrol and diesel as transport fuels in several countries and this process is likely to accelerate as oil prices rise. Mohapatra (M-1) has also reported that the Government of India is likely to soon come out with a comprehensive policy regarding Biodiesel. It can be pointed out that with growing environmental concerns, many developed countries of the world are going in for biodiesel. In June 2001, St. Louis in the United State decided to run city buses on soybean-based Biodiesel. As the world is caught between twin growing problems arising out of depleting fossil fuel reserves and environmental degradation due to exhaust emissions; Biodiesel is one such fuel, which is capable of providing a ready Solution to this twin crisis. Singh R. P. (S-3) has also recently reported that Palm oil will be a newer and non-conventional source of vehicle fuel in India.

1.2.1 Biodiesel Raw Material

The main and basic raw material for the production of biodiesel is a vegetable oil derived from oilseeds. Hegde D.M. and Kiresur V. (H-1) have reported that the dramatic transformation of the Indian oil seeds economy from a "net importer" status in the Eighties to a "Self-sufficient" and "net exporter" status during the early nineties has been popularly termed as the "Yellow Revolution". From a mere 11 million tonnes during 1986-87, the country attained a record oilseed production of 25 million tonnes during 1996-97, just in the Span of a decade.

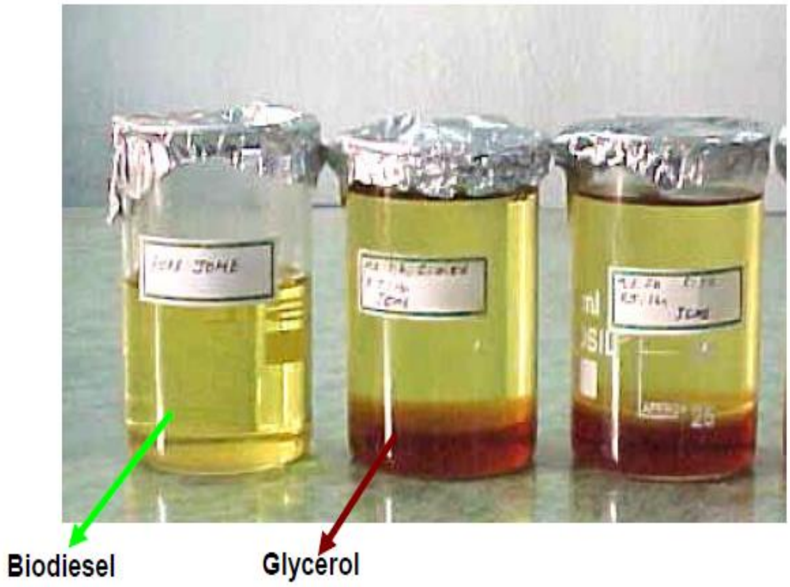
The main contributors to such significant transformation are the oilseeds production technology, the expansion in cultivated areas, the price support policy and the institutional support, particularly the formation of the Technology Mission on Oilseeds in 1986, among others. India has reached this level of production mainly by the efforts, of the Technology Mission and the series of synergistic and farmer-oriented policies it has launched backed up by better availability of crop production technologies and other inputs and services as well as support price policy, the country witnesses a spurt in oilseeds production touching a record of about 25 million tonnes during 1996-97. This is considered sufficient to meet the domestic demand and to some extent the export demand.

During the last two decades, over 240 improved varieties/ hybrids have been developed in annual oilseeds, which have 9.0 to 38 per cent yield superiority over their locally cultivated counterparts. However, there is scope to evolve varieties/hybrids, which can give 50 per cent or evermore yields in on-farm conditions.

The annual vegetable oil seeds are cultivated in 14 states of which eight, namely, Madhya Pradesh, Rajasthan, Andhra Pradesh, Uttar Pradesh, Gujarat, Karnataka, Maharashtra and Tamil Nadu account for nearly 90 per cent of the oilseeds area and production in the country. Madhya Pradesh shares the highest area and production, followed by Rajasthan, Andhra Pradesh and Gujarat. Among different oilseeds, rape-seeds-mustard happen to be the major oilseed crop in seven states, groundnut in four states, soybean sesame and niger in one state each.

1.2.2 Production of Biodiesel

Biodiesel is produced by crushing oilseeds, filtering the oil to remove all impurities and gum and then heating it to 60°C with alcohol, using caustic soda as a catalyst. This process is known as _ transesterification, which removes triglyceride molecules from vegetable oil in the form of glycerine a premium industrial chemical leaving biodiesel. The selling price of biodiesel is expected to be between Rs. 75.00 to Rs. 85.00 per litre.



2. Experimental Programme

2.1 Material Used

For the synthesis of methyl ester from vegetable oils following were the requirements of chemicals for the purpose. The use of the alkali (KOH) was as a catalyst required for the transesterification.

Sr. No	Chemical	Grade	Manufactured by
1	Sodium hydroxide (NaOH) Pellet	AR	Qualigens Fine Chemical
2	Potassium hydroxide (KOH) Pellet	LR	Ranbaxy Laboratories Limited
3	Methanol Extra Pure	-	E. Merck India Ltd.
4	Potassium Dichromate ($K_2Cr_20_7$)	AR	Central Drug House (P) Ltd.
5	Sodium Thiosulphate ($Na_2S_20_3$ $5H_20$)	-	Glaxo Laboratories (India) Ltd.
6	Phenolphthalein	LR	S.d. Fine-Chemical Pvt. Ltd
7	Rectified Spirit	-	-

The vegetable oils used for the experimental work are the sunflower oil procured from the M/s. Agrotech Food Ltd. used sunflower oil, mustard oil of Dhara, Vegetable Oil & Food Co. Ltd. and used mustard oil. All the above experimental oilseeds have been analysed for their physicochemical characteristics viz., Density acid value, free fatty acid, viscosity, kinematic viscosity, water content flash point, pour point, calorific value, iodine value, saponification value and carbon residue, The values obtained have been reported in Table 3.1, 3.2, 3.3 and 3.4 for sunflower oil, used sunflower oil, mustard oil and used mustard oil respectively. For characterizing these oils, the test procedures given in BIS specifications have been followed.

2.2 CALCULATION OF METHANOL AND CATALYST QUANTITY FOR THE REACTION

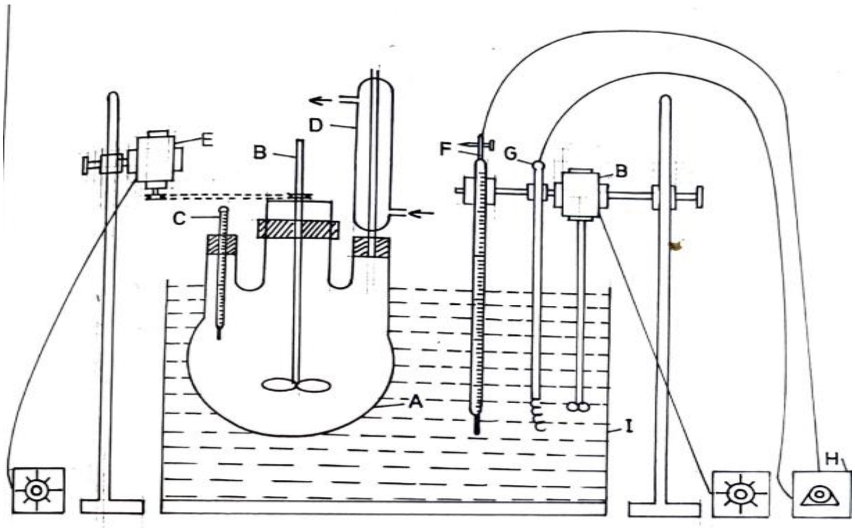
In the transesterification reaction for the preparation of methyl ester from the experimental vegetable oils, the amount of methyl alcohol was initially calculated based on the formula given by Charles L.

Peterson etal. (C-4) i.e. MeOH = 0.225 x oil, where oil represents the actual quantity of experimental oil taken in grams in each experiment, respectively.

The catalyst potassium hydroxide KOH was calculated by equation KOH = Oil/100, where, oil is the amount of vegetable oil taken in the transesterification reaction.

2.3 EXPERIMENTAL SETUP

The experimental setup for the investigations has been given in fig. 3.1. The setup consists of a round bottom flask of 1.0litre capacity provided with three standard joint openings. The first opening was used for putting the thermometer to monitor the temperature, and the second one was used to fit the condenser. The central opening was provided with a stirrer for continuous agitation of the contents of the flask. About 2/3 portion of the flask was dipped in a water bath capable of being maintained at a constant temperature with the help of a thermometer and relay.



EXPERIMENAL SET UP OF TRANSESTERIFICATION

Where;

A= Round Bottom Flask B = Stirrer regulator

C = Thermometer D= Condenser

E = Stirrer with multipurpose speed regulator F = Constant Thermometer

G= Immersion Rod H = Relay

I = Water Bath

2.4 Experimental Procedure

The required quantity of experimental oil i.e. raw and used sunflower oil and mustard oil was placed for transesterification reaction for the production of methyl ester biodiesel, separately in the round bottom flask in this experimental study. A calculated amount of KOH dissolved in a fixed quantity of methanol was added to the flask having experimental oil. The temperature was maintained with the help of a water bath. The reaction mixture was stirred for 60 minutes, vigorously as vegetable oil and methanol are not miscible. The stirred material (mixture) is then transferred to a separating funnel and left for ~18 hours for the phase separation. The bottom layer formed consists of glycerol and methanol and the upper layer has methyl ester, biodiesel of respective experimental oil used.

In this study effect of temperature on the yield of methyl ester was studied by varying the temperature of the reaction vessel to three different temperatures. ie. 50°C, 60°C, 70°C, 80°C & 90°C. On getting the maximum yield of methyl ester the temperature of the reaction was decided for subsequent experimental work.

The methyl alcohol proportion was also varied to assess the effect of methyl alcohol proportion in reactants.

RESULT AND DISCUSSION:

Table: Comparative study of some important quality characteristics of BIS requirement for Diesel. Fuel and methyl ester biodiesel are formed from different experiment oils

S.No	**Characteristics**	**BIS Requirements for diesel fuels (Is:1460 :2000)**		**Methyl ester, biodiesel of experimental**			
		HSD	**LDO**	**Sunflower oil**	**Used sunflower**	**Mustard oil**	**Used mustard oil**
1	Water content vol % max	0.05	0.25	0.04	0.05	0.07	0.05
2	Acidity total mg of KOH/g max	0.20	-	0.12	0.15	0.16	0.18
3	Dencsty kg/m^3	820-860	-	883	873	877	888
4	Kinematic viscosity cSt at 40^{o}C	2.0-5.0	2.5-15.7	4.782	3.870	4.468	4.542
5	Flashpoint ^{o}C min	35	-	190	156	154	112
6	Distillation range ^{o}C (% v/v recovered)						
	10%	-	-	286	281	237	285
	50%	-	-	292	283	304	305
	85%	350	-	351	350	352	351
	90%	-	-	353	351	356	352
	95%	370	-	372	374	368	370
7	Pour point max ^{o}C (Subject to seasonal change)	3-15	12-21	9	6	12	9
8	Calculated Cetane No. mim	46-48	-	47.40	47.6	47.6	45.8
9	Carbon Residue (Rams- bottom) on 10% residue % by mss max	0.30	1.5 on whole semple	1.42	1.48	1.46	1.47

CONCLUSION:

In the present research work, the experiments were performed to convert raw and used sunflower oil and mustard oil, of their; respective methyl esters, bio-diesel through a transesterification reaction. The conversion was found to be dependent on mainly three factors i.e., reaction temperature, the proportion of methyl alcohol in reactants and the amount of catalyst (KOH) i.e., alkali used.

Therefore, the transesterification reaction for experimental oil was carried out at different temperatures i.e., 50, 60, 70, 80 & 90°C and their respective yield of methyl ester biodiesel was recorded. The maximum yield obtained was 92.24%, 91.12%, 91.23% and 93.78% for raw sunflower oil, used sunflower oil, raw mustard oil, and used mustard oil, respectively, at 70°C. Hence, it could be recommended that for transesterification reaction in the production of methyl ester, bio-diesel from raw & used plant oils. The optimum reaction temperature for maximum yield is 70°C.

Likewise in the optimization of methyl alcohol proportion in the transesterification reaction, the quantity of Methyl alcohol varied as 0.175 x oil, 0.20 x oil, 0.225 x oil, 0.250 x oil and 0.275 x oil, respectively, at an optimum reaction temperature of 70°C. The yield of methyl ester obtained was assessed and it was concluded that the proportion of methyl alcohol as 0.225 x oil can be taken as optimum for the production of maximum yield of methyl ester biodiesel.

Following optimization of reaction temperature & methyl alcohol proportion for maximum conversion of experimental oil to their respective methyl ester yield, the experiment was carried out to assess the effect of varying amounts of catalyst i.e., alkali (KOH) used. The amount of catalyst (KOH) used varied as oil/80, oil/90, oil/100, oil/110 and oil/120, respectively. The yield thus obtained was observed as maximum yield of methyl ester at 70^{o}c with methyl alcohol proportion of 0.225 x oil & optimum catalyst quantity as oil/100.

The comparative study of quality characteristics of diesel fuel: BIS vis-a-vis property of synthesizing methyl ester biodiesel were also made for water content, density, kinematic viscosity flash point, distillation range, pour point, Cetane no. and carbon residue etc. which influences the ultimate quality of fuel. The value obtained for these parameters were almost in the range of the prescribed limit.

It is finally concluded that the methyl ester bio-diesel obtained from all four oil samples use at the optimum condition of reaction temperature (70°C), methyl alcohol proportion (0.225 x oil)to oil and quantity of alkali (KOH) used (oil/100) as a catalyst worked out during the investigation conform to the BIS requirement and have values well with-in the range prescribed for diesel fuel. Therefore, the product synthesized can be used & be acceptable as a substitute for diesel fuel. Its use directly or as a blend in certain proportions, if encouraged in India, can save a lot of our foreign exchange reserves, which we have to spend on buying Petroleum and petroleum products.

Following optimization of reaction temperature & methyl alcohol proportion for maximum conversion of experimental oil to their respective methyl esters yield, the experiments were carried out to assess the effect of varying amounts of catalyst i.e., alkali (KOH) used. The amount of catalyst (KOH) used was varied as oil/80, oil/90, oil/100, oil/110 and oil/120, respectively. The yield thus obtained was observed as a maximum yield of methyl ester at 70°C with methyl alcohol Proportion of 0.225 x oil & optimum catalyst quantity as oil /100.

The comparative study of quality characteristics of diesel fuel: BIS vis-a-vis properties of synthesized methyl ester biodiesel were also made for water content, density, kinematic viscosity, flash point, distillation range, pour point, cetane no. and carbon residue etc. which influences the ultimate quality of fuel. The value obtained for these parameters were almost in the range of the prescribed limit.

It is finally concluded that the methyl ester bio-diesel obtained from all the four oil samples used at the optimum conditions of reaction temperature (70°C), methyl alcohol Proportion (0.225 x oil) to oil and quantity of alkali (KOH) used (oil/100) as a catalyst worked out during the investigation to the BIS requirement and have values well within the range prescribed for diesel fuel. Therefore, the product synthesized can be Used & be acceptable as a substitute for diesel fuel. Its use directly or as a blend in certain proportions, if encouraged in India, can save a lot of foreign exchange reserves, which we have to spend on buying Petroleum and petroleum products.

REFERENCES:

A-1 Anon Danik Jagran p.13 Kanpur Edition Dated Aug. 30, (2002).

A-2 Anon www.afdc.doc.gov/allfuel (1998).

C-1 Chandra A. Oil Exploration: New bids bring hope p.149 The Hindu-Survey of Indian Industry (2001).

C-2 Chakrabarti P.P. Innovative Products from the vegetable oils for the 21st Century. The Journal of OTAI, Vol. 31, 4, p. 203 Oct.-Dec. 1999

C-4 Charles L. Peterson Production and Testing of Ethyl and Methyl Esters www.afdc.doc.gov/all fuel (1994).

H-1 Hegde D.M. and Kiresur V. Oil Seeds: Changing Paradigms.The Hindu Survey of Indian Agriculture (1999).

M-1 Mohapatra S. A news article- Biodiesel policy to be out soon. The Hindustan Times New Delhi Edition June 24, (2002).

R-1 Rai, G.D. Non-conventional energy sources Khanna Publishers Delhi (1997).

R-2 Rao, P.S., and Gopal Krishnan, K.V. Indian Journal of Technology, 29, 292 (1991).

S-1 Srivastava A. & Prasad R. Transesterification of Raw and used vegetable oils. Indian Chem. Engg. Section B. Vol. 44, 2, Apr.-June (2002).

S-3 Singh R.P. Palm Oil - A non-conventional source of vehicle fuel new article: Amar Ujala NewsPaper Kanpur Sept. 3 (2002).