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BIO-DIESEL PRODUCTIVITY BY USING DIFFERENT ACIDS VIA ACIDS CATALYSIS AND ITS BLENDS WITH DIESEL

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Abstract: Biodiesel is renewable, non degradable, cleaner and efficient fuel for IC Engines. Conventionally it is produced by the alkali catalysis but due to more FFA contents in oils the Acid catalysis method is becoming popular for reserchers. In these reserch work the productivity of Diferent acids is evaluated for different concentrations of Acids, Methanol and catalysts for constant temperature and time is measured. The optimum combination Via Hydroclric Acid for Methanol /Pretreated oil, Acid concentration and Time wise is 0.16,1% and 28 min. Which gives yield upto 81% which meets ASTM Fuel requirements. The optimum combination Via Nitric Acid for Methanol /Pretreated oil, Acid concentration and Time wise is 0.20, 1.25% and 50 min. Which gives yield upto 92.734% which meets ASTM Fuel requirements. The optimum combination Via Sulfuric Acid for Methanol /Pretreated oil, Acid concentration and Time wise is 0.20, 1.5% and 24 min. This gives yield up to 99.009% which meets ASTM Fuel requirements.

Keywords: Acid Catalyst, Transestrification,

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INTRODUCTION

Exploring new renewable energy sources is the need of present fuel scenario, the petro-fuels are vanishing more rapidly to meet heavy demands of today's population. The Bio-fuels look attractive and inviting source in these situations. Bio-diesel of these categories have more environmental benefits and reduce carbon emissions by 85% compared to the petro-diesel. Combustion of bio-diesel is more proper than gasoline and diesel with less emissions of carbon monoxide, particulate matter and toxic chemicals[1].

Biodiesel is the product of the process known as 'Transesterification' in which Triglyceroids from oil react with alcohol under the action of certain catalysts at specific constant temperature for some time to produce bio-diesel as a result. Bio-diesel can be used in internal-combustion engine applications solely or blending with petro-diesel[2,3]. According to literature review, its blends show good performance and emissions characteristics. Their blend improves properties like Lubricity and stability etc.

Lots of benefits of using biodiesel: it is a renewable source, burns cleaner than petro-diesel and is compatible with petro-diesel. Bio-diesel can be produced through many techniques including Acid & Base catalysis, Enzymatic conversion, Solid catalysts, Non-catalytic conversion and Super-critical Methanolysis. Enzymatic conversions are expensive and unable to provide to meet ASTM Fuel specifications. For Solid catalysts, High pressure and temperature arrangements are required. Also for Non-catalytic conversion, Large set-up and Extreme operation conditions are required. So only base and acid catalysis are simple and feasible techniques for local researchers. Out of which when Free Fatty Acid contents are more than 5% then there will be more soap formation and wastage of base catalyst so it is unfavorable in such cases so remaining Acid catalysis is used when FFA content is more than 5% in feedstock oil.

This research is related to the method of bio-diesel production from acid catalysis in which Productivity of different Acids is evaluated. The Acids used are of AR (Analytical Reagent) quality including Hydrochloric acid, Nitric Acid and Sulfuric Acid.

2. EXPERIMENTAL

2.1 Chemical: All the chemicals used are of Analytical Reagent (AR) quality which includes use of conc. hydrochloric acid (HCl), conc. nitric acids (HNO₃), conc. sulphuric acids (H₂SO₄), sodium hydroxide pellets, Methanol etc.

2.2 Properties of used oil:

Oil PH: - 50 ml beaker is used in which 2 gm of sample oil was poured and 25 ml distilled water added in it and stirred slowly. Then it is cooled upto 25^oc in water bath. The PH electrodes are immersed into solution and PH value measured from digital meter after stability.

Oil Viscosity:-It is measured by 'Redwood Viscometer' consist of steel two steel container, one is outer and other is inner. The diameter of outer container is greater than inner, and there having an empty space between the two. The empty space consist of hot water which surrounds the inner container containing oil in that. The water is heated by heating coil. The oil absorbs heat from surrounding hot water by convection. The oil container have very small hole at the bottom so that oil can drop through that hole. As we got required temperature on the temp. indicator, the small diam. rod was removed to allow the oil fall down in volume measuring flask. It was required to measured that how much time taken by oil to fill 50 ml in volume measuring flask. And viscosity was calculated from the following constants and formula.

$$\text{Viscosity} = A * t - \frac{B}{t}$$

Where, A=0.26, B=17, t= time

2.3 Preparation of oil for biodiesel production:

The oil is filtered to remove any impurity, foreign partical and debris present. The oil is heated at 100^oc for 30 min to remove water and improve reactivity of oil .The amount of water should be less than 0.04%(wt%) .Then only the standard limit of water content is fulfilled .water is very dangerous for acid catalysis it may disturb or even stop the bio-diesel production.

2.4 Preparation of NA-O-CH₃ for biodiesel production:

Silica Granule is used to dry the methanol and finally it is deepfreeze. The potassium hydroxide (AR) surface is cleaned by steel knife and its weight is measured quickly. Then KOH is dipped in 100 ml methanol containing beaker .The 'The magnetic rotor machine' is used to completely dissolve the KOH in methanol to form NA-O-CH₃ solution in desired concentration.The stirring was done upto 15-20 min to form more homogeneous solution.

2.5 Complete Protocol for Biodiesel Production.

Initially the raw waste cooking oil is heated upto 60^o C which improves the reactivity of oil and gives better results .

Then the oil is pretreated to reduce FFA content by treating it one by one with strong Acids e.g. HCL, HNO₃, H₂SO₄ etc these solution is heated and stirred vigourously at constant temperature of 70⁰ C for 60 minutes for maintaining the constant temperature water bath is used and mechanical stirrer used for stirring .

Then the PH of pretreated oil is check which is must be 6 to 7 if it is not then the heating time of solution is extended . The PH is checked by PH analyser by simply inserting its probes in solution The digital meter gives the reading of PH .Pretreated oil is ready to use now.

The Centrifuging machine is used to remove the FFA from raw oil . the centrifuging machine is operated at 5200 RPM for 20 Minutes.The FFA level formed at upper portion which can easially remove.These is pioneering step for reserchers working on biodiesels.the lower portion can now be used for biodiesel production.

Sodium Hydroxide pallets is added in Methanol and stirred vigourously for some time to form sodium Methoxide .The Magnetic Rotor Machine is used for these purpose in which magnetic rotor is dipped in methanol contained beaker the machine frequently changes magnetic field which tends to rotate the magnetic rotor which then stirred the mixture vigourously.

These produced Sodium Methoxide is treated with Pretreated oil which having less FFA contents e.g.by alkali catalysis method at constant temperature of 60⁰ C and stirred vigourously in water bath by mechanical stirrer. Generally the biodiesel formation starts from first 20 min the biodiesel samples taken for testing after each five min onwards to analysed the properties to check quality and meet ASTM fuel Requirements .Then the best samples are choosen on the basis of properties obtained through impirical analysis.

The Centifuging machine used finnaly to remove glycerin and if any catalyts. impurity and foreign particals are presents .

The tastes are taken one by one for following Acids HCL, HNO₃, H₂SO₄ .the found result as follows

3 RESULTS AND CONCLUSIONS

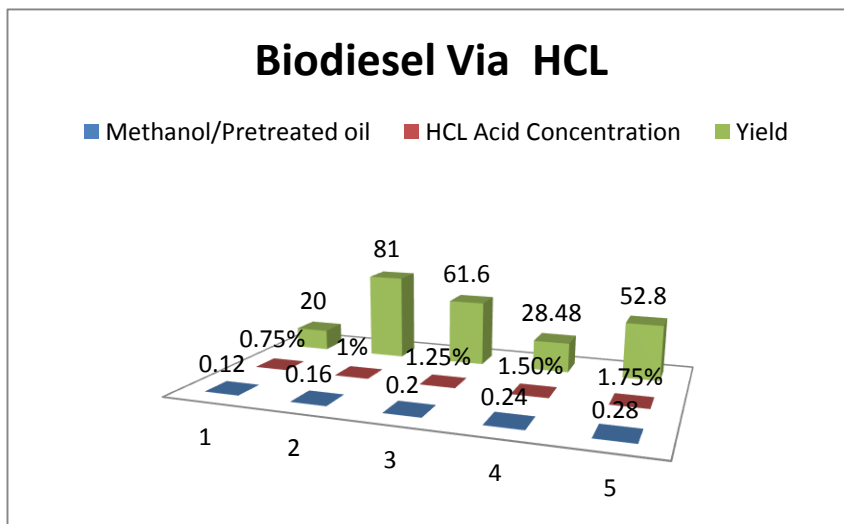


Fig 3.1 (a):- Biodiesel Processes Via HCL

S.N	Methanol/ Pretreated oil	Acid Concentration	Temp (°C)	Time	Yield (%)	Glycerin (Wt)	Viscosity As tm 1.9-6.0	CV	Flash point	Fire point	TAN	Results
HCL												
1	0.12	0.75%	60	35	20	21.67	7.11	41122	167	173	0.5122	For time upto 25 min NO formation of BD After 45 min more viscous & unacceptable BD form .
2	0.16	1%	60	28	81	6.67	5.08	42800	148	157	0.5125	BD form after 20 min and mostly acceptable upto 40 after more viscous BD form.
3	0.20	1.25%	60	68	61.6	8.11	9.54	38522	159	167	0.5636	BD form in some minutes but viscous and unacceptable & heating time hence Increased.
4	0.24	1.50%	60	55	28.48	19.96	10.45	39855	167	173	0.5989	BD form in some minutes but viscous and unacceptable.
5	0.28	1.75%	60	43	52.8	14.62	12.33	36555	168	175	0.6124	BD form in some minutes but viscous and unacceptable.
HNO3												
6	0.12	0.75%	60	90	79.33	15.48	3.98	42556	162	171	0.4172	BD Form after 70 min less viscous

7	0.16	1%	60	62	81.06	12.76	4.12	40235	165	173	0.4898	but not meet ASTM .
8	0.20	1.25%	60	50	92.73	8.89	4.59	41222	157	152	0.5012	BD Form after 55 min less viscous but not meet ASTM.
9	0.24	1.50%	60	45	50.63	26.142	6.98	41235	171	180	0.5986	BD Form after 40 min less viscous And meets ASTM.
10	0.28	1.75%	60	36	40.07	31.39	7.33	42512	173	181	0.6123	BD Form after 20 min more viscous.
H2SO4												
11	0.12	1%	60	45	90.84	18.60	5.68	42536	159	168	0.5124	BD Form emidiatly but more viscous.
12	0.16	1.25%	60	40	94.72	14.36	6.25	41988	168	175	0.5235	BD Form after 20 min but poor qual upto 40Above good upto 90 min and then viscous.
13	0.20	1.50%	60	24	99.00	11.58	3.99	40235	154	161	0.5350	BD Form after 15 min but poor quality.
14	0.24	1.75%	60	65	95.06	13.92	6.11	45889	171	178	0.5981	BD form emidiatly after 40 min visco increases drastically.
15	0.28	2.00	60	88	98.17	12.36	7.14	43566	169	176	0.6315	BD form immediately but unacceptable.

TABLE:- Productivity of Different Acids

3.1 Biodiesel Production Via HCL Acid

When HCL is used in different proportions and the results are studied is observed that Biodiesel (BD) is not formed upto 25 min and if we continue heating so after say 45 min unacceptable and viscous BD formed. The found best combination is Methanol /Pretreated oil , Acid concentration and Time wise is 0.16,1% and 28 min.Which gives yield upto 81% which meets ASTM Fuel requirements.Fig3.1(a)shows the optimum combination while Fig3.1(b) shows the Glycerin (Wt%) of Biodiesel process. Fig concludes that the sample 2 gives High yield with Low glycerin formation.

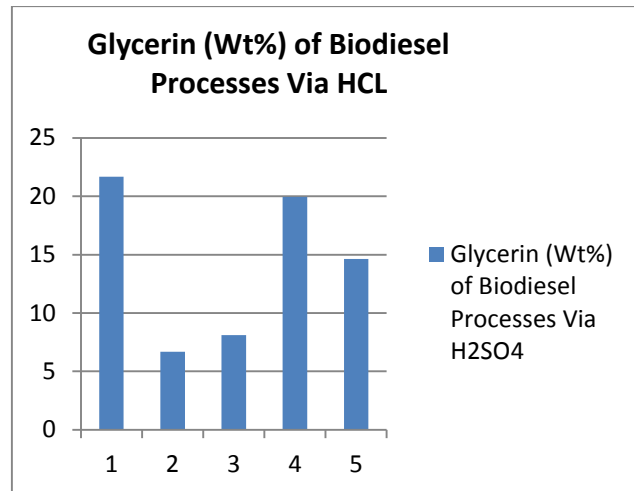


Fig 3.1 (b):- Glycerin (Wt%) of Biodiesel Processes Via HCL

3.2 Biodiesel Production via HNO_3 Acid

When HNO_3 is used in different proportions and the results are studied is observed that Biodiesel (BD) is formed after 40 min and if we continue heating and increased Acid concentration BD form faster but unacceptable and viscous BD formed. The found best The optimum combination Via Nitric Acid for Methanol /Pretreated oil , Acid concentration and Time wise is 0.20,1.25% and 50 min.Which gives yield upto 92.734% which meets ASTM Fuel requirements..Fig3.2 (a) shows the optimum combination while Fig3.2 (b) shows the Glycerin (Wt %) of Biodiesel process. Fig concludes that the sample '3' gives High yield with Low glycerin formation.

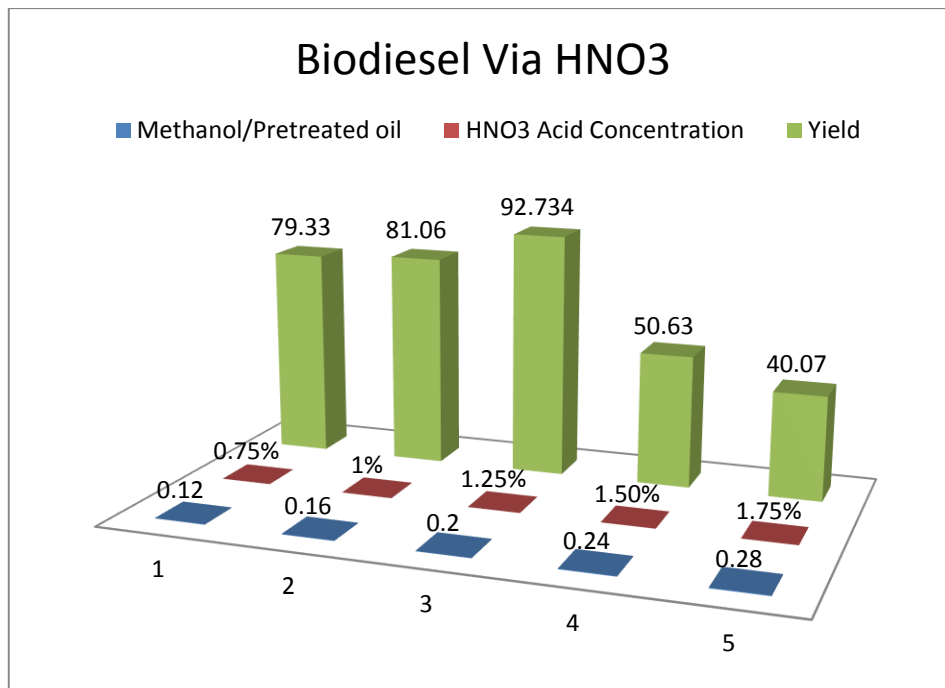


Fig 3.2 (a):- Biodiesel Processes Via HNO₃

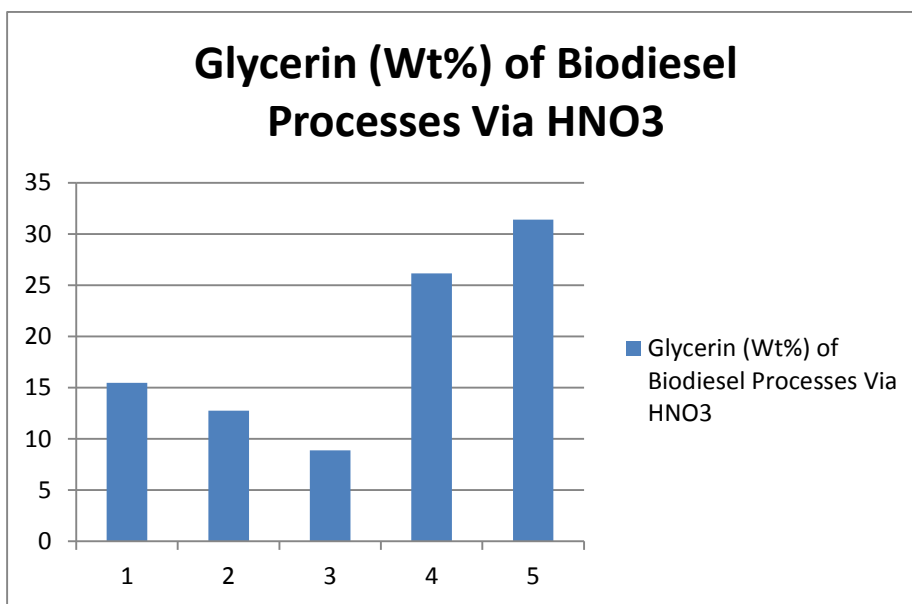


Fig 3.2 (b):- Glycerin (Wt %) of Biodiesel Processes Via HNO₃

3.3 Biodiesel Production via H₂SO₄ Acid

When H₂SO₄ is used in different proportions and the results are studied it is observed that Biodiesel (BD) is formed after 20 min and if we continue heating and increased Acid concentration BD form faster but unacceptable and viscous BD formed. The found best optimum combination Via Sulfuric Acid for Methanol /Pretreated oil , Acid concentration and Time wise is 0.20,1.5% and 24 min.Which gives yield upto 99.009% which meets ASTM Fuel requirements..Fig3.3 (a) shows the optimum combination while Fig3.3 (b) shows the Glycerin (Wt %) of Biodiesel process. Fig concludes that the sample '3' gives High yield with Low glycerin Formulation

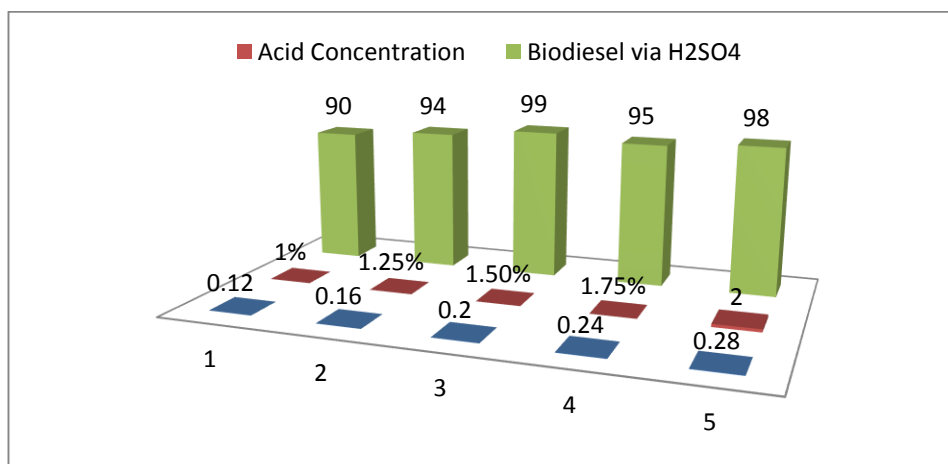


Fig 3.3 (a):- Biodiesel Processes Via H₂SO₄

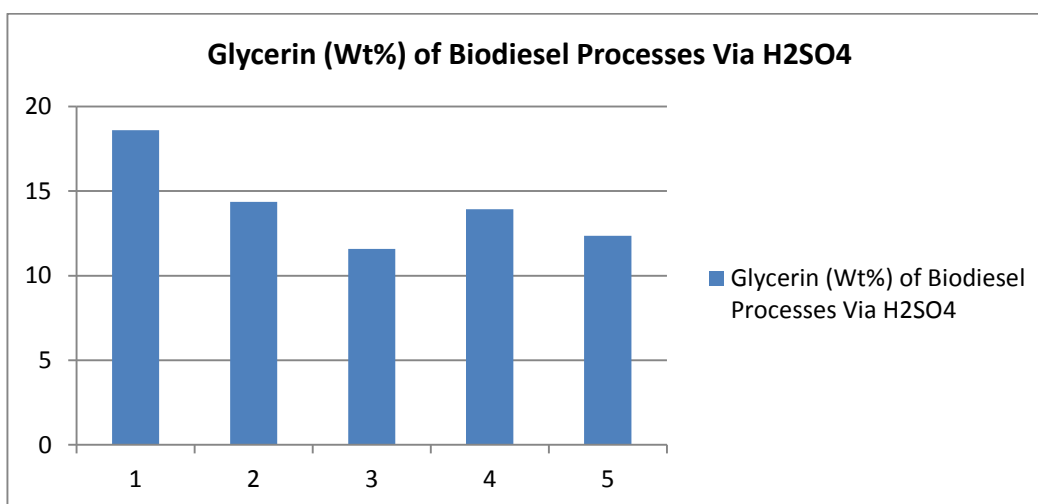


Fig 3.3 (b):- Glycerin (Wt%) of Biodiesel Processes Via H₂SO₄

3.4 Biodiesel Production Comparison for different Acids.

The Biodiesel production Via H_2SO_4 gives High yield than other Acids. The properties of BD via H_2SO_4 is good but the BD produced via HCL also shows good results in consideration through yield wise and properties wise which is achievement of the experimentation done.

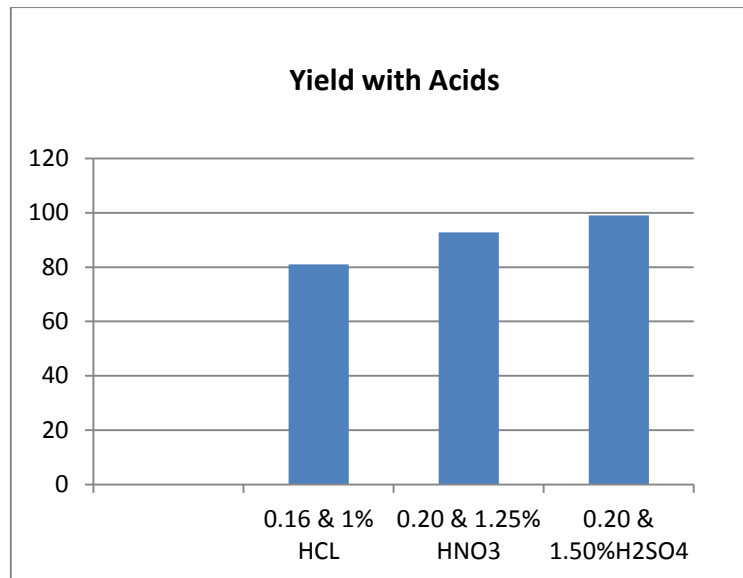


Fig 3.4: Yields with Different Acid

4. CONCLUSION:-

- 1) The optimum combination Via Hydrochloric Acid for Methanol /Pretreated oil, Acid concentration and Time wise is 0.16, 1% and 28 min. Which gives yield up to 81% which meets ASTM Fuel requirements.
- 2) The optimum combination Via Nitric Acid for Methanol /Preated oil, Acid concentration and Time wise is 0.20, 1.25% and 50 min. Which gives yield up to 92.734% which meets ASTM Fuel requirements.
- 3) The optimum combination Via Sulfuric Acid for Methanol /Preated oil, Acid concentration and Time wise is 0.20, 1.5% and 24 min. Which gives yield up to 99.009% which meets ASTM Fuel requirements.
- 4) The productivity of sulfuric acid is highest, the Nitric Acid is moderate while Hydrochloric acid is lowest yield wise. The biodiesel produced via Hydrochloric acid has good fuel properties than nitric Acids.

5. REFERENCES

1. Sastry GSR, Krishna Murthy ASR, Ravi Prasad P, Bhuvanewari K, Ravi PV. Identification and determination of bio-diesel in Diesel. *Energy Sources Part A* 2006;28:1337–42.
2. Demirbas A. Biodiesel fuels from vegetable oils via catalytic and noncatalytic supercritical alcohol transesterifications and other methods: a survey. *Energy Convers Manage* 2003;44:2093–109.
3. Knothe G, Dunn RO, Bagby MO. Biodiesel: the use of vegetable oils and their derivatives as alternative Diesel fuels. *Am Chem Soc Symp Series* 1997;666:172–208.
4. Ryglewicz S. Rapeseed oil methyl esters preparation using heterogeneous catalysts. *Biores Technol* 1999;70:249–53.
5. Furuta S, Matsushashi H, Arata K. Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure. *Catal Commun* 2004;5:721–3.
6. Hama S, Yamaji H, Kaieda M, Oda M, Kondo A, Fukuda H. Effect of fatty acid membrane composition on whole-cell biocatalysts for biodiesel-fuel production. *Biochem Eng J* 2004;21:155–60.
7. Oda M, Kaieda M, Hama S, Yamaji H, Kondo A, Izumoto E, et al. Facilitatory effect of immobilized lipase-producing *Rhizopus oryzae* cells on acyl migration in biodiesel-fuel production. *Biochem Eng J* 2004;23:45–51.
8. Shieh C-J, Liao H-F, Lee C-C. Optimization of lipase-catalyzed biodiesel by response surface methodology. *Biores Technol* 2003;88:103–6.
9. Nouredini H, Gao X, Philkana RS. Immobilized *Pseudomonas cepacia* lipase for biodiesel fuel production from soybean oil. *Biores Technol* 2005;96:769–77.
10. Demirbas A. Biodiesel fuels from vegetable oils via catalytic and noncatalytic supercritical alcohol transesterifications and other methods: a survey. *Energy Convers Manage* 2003;44:2093–109.
11. Demirbas A. Biodiesel from vegetable oils via transesterification in supercritical methanol. *Energy Convers Manage* 2002;43:2349–56.
12. Nouredini H, Gao X, Philkana RS. Immobilized *Pseudomonas cepacia* lipase for biodiesel fuel production from soybean oil. *Biores Technol* 2005;96:769–77.

13. Barnwal BK, Sharma MP. Prospects of Biodiesel production from vegetable oils in India. *Renew Sust Energy Rev* 2005;9(4):363–78.
14. Srivastava A, Prasad R. Triglycerides-based diesel fuels. *Renew Sust Energy Rev* 2000;4:111–33.
15. Ma F, Hanna MA. Biodiesel production: a review. *Bio resource Technology* 1999;70:1–15
16. Ma F, Hanna MA. Biodiesel production: a review. *Bioresource Technol* 1999;70:1–15.
17. Fukuda H, Kondo A, Noda H. Biodiesel fuel production by transesterification of oils. *J Biosci Bioeng* 2001;92(5):405–16.
18. Barnwal BK, Sharma MP. Prospects of Biodiesel production from vegetable oils in India. *Renew Sust Energy Rev* 2005;9(4):363–78.
19. Zhang Y, Dube MA, McLean DD, Kates M. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technol* 2003;89:1–16.
20. Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from transesterified vegetable oils. *JAOCS* 1984;61(10):1638–43.
21. Nouredini H, Zhu D. Kinetics of transesterification of soybean oil. *JAOCS* 1997;74(11):1457–63.
22. Freedman B, Butterfield R, Pryde E. Transesterification kinetics of soybean oil. *JAOCS* 1986;63(10):1375–80.
23. Mittelbach M, Tratnigg B. Kinetics of alkaline catalyzed methanolysis of sunflower oil. *Fat Sci Technol* 1990;92(4):145–8.
24. American Society for Testing and Materials, Standard Specification for Biodiesel Fuel (b100) Blend Stock for Distillate Fuels, Designation D6751-02, ASTM International, West Conshohocken, PA, 2002
25. Y. Shimada, Y. Watanabe, T. Samukawa, A. Sugihara, H. Noda, H. Fukuda, Conversion of vegetable oil to biodiesel using immobilized *Candida antarctica* lipase, *JAOCS* 76 (7) (1999) 789–793.
26. W.H. Wu, T.A. Foglia, W.N. Marmer, J.G. Phillips, Optimizing production of ethyl esters of grease using 95% ethanol by response surface methodology, *JAOCS* 76 (4) (1999) 517– 521.

27. G.I. Keim, Treating fats and fatty oils, U.S. Patent No. 2,383,601, Awarded (Aug. 28, 1945).
28. Freedman B, Pryde EH, Mounts TL. Variables affecting the yields of fatty esters from vegetable oils. *JAOCS* 1984;61(10):1638-43.
29. Freedman B, Butterfield R, Pryde E. Transesterification kinetics of soybean oil. *JAOCS* 1986;63(10):1375-8
30. Harrington KJ, Darcy-Evans C. *Ind Eng Chem Prod Res Dev* 1985;24:314.
31. Debirmas A. Fatty and resin acid recovered from spruce wood by supercritical acetone extraction. *Holzforschung* 1999;45:337-9
32. Schelenk H, Gellerman JL Esterification of fatty acid with diazomethane on small scale. *Anal chem* 1960;32:1412-4
33. Christie WW. *Gas chromatography and lipids: a practical guide*. Dundee: The Oily Press; 1989
34. Demirbas A. Biodiesel from vegetable oils via transesterification in supercritical methanol. *Energy Convers Manage* 2002;43:2349-56.
35. J. Sheehan, V. Camobreco, J. Duffield, M. Graboski, and H. Shapouri Life cycle inventory of biodiesel and petroleum diesel for use in an urban bus, final report for U.S. Dept. of Energy's Office of Fuel Development and the U.S. Dept. of Agriculture's Office of Energy, by the National Renewable Energy Laboratory, NREL/SR-580-24089 (May 1998).