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Optimization of process of biodiesel produced via Acid catalysts using Sulfuric Acid, Hydrocloric acid and Nitric acid.

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Abstract- *The consumption of nonrenewable resources like petroleum fuels is on peak and increased exponentially in past decades, the supply of such resources may end after few decades. The harmful effects pollution, green house gases increasing very rapidly. The development of renewable, cleaner and safer energy sources is an essential to survive. Total energy indepence on petroleum based fuels by development of biodiesel may become possible. In the present work biodiesel is produced by Waste Cocking oil (WCO) by acid catalysis followed by conventional base catalysis. Free Fatty Acid (FFA) level is increased after each fry in cooking oil which increases cancerous and unhealthy chemicals. If such higher FFA level waste fried oil directly used for biodiesel production via conventional base catalysis tends to more soap formation and wastage of base catalyst which in terms difficult the separation of glycerin and biodiesel production. By using acid catalyst the FFA level can be reduce considerably and biodiesel can be produce by base catalysis. In the present work, different acid catalysts like Sulfuric acid, Hydrocloric acid and Nitric acid are used for the biodiesel production.*

Keywords: biodiesel, acid catalysis, Base Catalysis

I.INTRODUCTION

Biodiesel produced from the transesterification of Vegetable liquids oils or Fats of animals and Alcohols can be potentially utilize in internal combustion diesel engines. American Society for Testing and Materials International defines biodiesel as product of fatty acid in a form of long-chain monoalkyl esters, which has potency to use in diesel engines. Blends i.e. mixture of Petro-diesel and biodiesel expressed as ‘‘Bx’’, where ‘‘x’’ is the biodiesel percentage. For example, ‘‘B15’’ expressed a blend with 15% biodiesel and 85% Petrodiesel fuel. B0 means pure petro-diesel.

One day complete energy independence through the progress of biodiesel technology may possible.

A. *Benefits of Biodiesel*

1. Renewable fuel, can be from vegetable liquid oils or fats of animals.
2. Less toxicity, with compared to petrodiesel fuel.
3. More rapidly degrades as compared to petrodiesel, less environmental pollution.
4. Lower emissions of gases: CO, PM, polycyclic, aromatic hydrocarbons, aldehydes.
5. Lower emission of carcinogenic matter, reduced health risk.
6. Zero sulfur dioxide (SO2) emissions.
7. Grater flash point (100^0C minimum).
8. Potency to burn in form of blends with petrodiesel and can be used to run vehicle.
9. Excellent lubricant.
10. Potency to use as a fuel without modifications in present diesel engine.
11. It can be produced from Waste Cooking Oil.

B. *Disadvantages Biodiesel*

1. Fuel consumption is slightly more due to the lower calorific value of biodiesel.

2. NO_x emission is more compared to petro-diesel engines.
3. Grater freezing point than diesel fuel. This is most important for cold climates.
4. Less stable, oxidized so cant preferably stored more than six months.
5. Degrade gaskets plastic and rubber. This can be overcome by using Teflon Components.

C. *Biodiesel production process*

Biodiesel is product of chemical reaction called esterification of vegetable oil (or animal fat). Biodiesel is produced from the process of purification of FAME (Fatty Acid Methyl Ester).Micro-emulsions, Pyrolysis and Transesterification are the methods of producing biodiesel. Treatment of raw materials, Alcohol-catalyst mixing, chemical reaction, Separation of the reaction products and Purification of the reaction products are the five steppes of Transesterification Process.

II LITERATURE REVIEW

Biodiesel processing and production (2007) University of Idaho, Moscow USA.Biodiesel Production Techniques are Acid catalysis, Base Catalysis, Enzymatic conversion,Solid catalysts, Non catalytic conversion, Super-critical Methanolysis. Enzymatic conversions are expensive and unable to provide to meet ASTM Fuel specification.For Solid catalysis High pressure and temperature arrangements are required. Non catalytic conversion Large set-up and Extreme operation conditions are required Only base and acid catalysis are simple and feasible techniques to 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 are more than 5% in feedstock oil.These paper concluded benefit of using acid catalyst for low cost high free fatty acid contained feed stock. In future scope Paper showed that Pretreatment processes using strong acid catalysts have been shown to provide good conversion yields and high-quality final products [9]

Comparison of transesterification methods for production of biodiesel from vegetable oils and fats .These Paper concluded that the use of Phosphoric and sulphonic acid as catalyst for the biodiesel production is beneficial [13].Use of Acid for Neutralization but a residual acid value equivalent to about 5% palmitic acid. The incomplete reaction was probably due to water in the reactant mixture. As shown in the reaction, water is formed, and if it accumulates, it can stop the reaction well before completion [5].

Possible methods for biodiesel production.Noureddini et al. have obtained good transesterification kinetics for acid catalyzed reaction for soybean oil [15].Biodiesel Production via Acid Catalysis. Acid-catalyzed transesterification is much slower than alkali-catalyzed. The ester conversion efficiency is strongly affected by the molar ratio of alcohol to oil. In esterification, a higher molar ratio is required than acid-catalyzed that of alkali-catalyzed. If the acid catalyzed reaction occurs at room temperature, the reaction is very slow and poor ester conversion is obtained. The completeness of ester formation increases with increasing acid catalyst amount. The ester conversion is strongly inhibited by the presence of water in the oil. If the waterconcentration is greater than 0.5%, the ester conversion rate may drop below 90% [10].

Transesterification kinetics of soybean oil. JAOCSFreedman and Pryde get the desirable product with 1mol% of sulfuric acid with a molar ratio of 30:1 at 65^{o}C and they get 99% of conversion in 50 h, while the butanolysis will need 117^{o}C C and the ethanolysis 78^{o}C but the times should be 3 and 18 h, respectively [3].Both constituents the fatty acid(oil) and alcohol i.e. methanol, can have considerable influence on fuel properties such as cetane number with relation to combustion and exhaust emissions, cold flow, oxidative stability, viscosity, and lubricity [8].

III SYSTEM DEVELOPMENT AND PRODUCTION PROCESS

A. *Significance of Acid Catalysis***.**

Conventional processing involves an alkali catalyzed process, but this method found to be unsatisfactory for feedstock which content high free fatty aciddue to soap formation but this feedstock is lower in cost. The cost associated with using enzyme catalyst is high and it is unable to meet specification, heterogeneous catalysts requires high pressure and

temperature conditions and Non catalytic as well as super critical methanolysis require large set-up and extreme operation conditions which required extreme engineering. In a competitive market the biodiesels must be economical, quick and continuous in production process compared to petrodiesel. In future, pretreatment processes using strong acid catalysts may be proven to provide good conversion yields and high-quality final products.

The acid catalysis is inviting method for producing bio-diesel. To evaluate the Productivity of biodiesel produced via Nitric Acid,Hydrochloric Acid and Sulfuric Acid is future scope for production of biodiesel. The present work is carried out using typical oil i.e. Waste Cocking oil as a fuel. However major disadvantage of Waste Cocking oil is its viscosity, which is order of magnitude higher that of petroleum based diesel. In the present work viscosity of Waste Cocking oil was reduced by transesterification process. Transesterification via Acid catalysis is done instead of Base Catalysis. Base Catalysis Proven Improper for FFA Level more than 5% which results in extra consumption of base catalysis and soap formations. Furthermore the different Acid Catalysts e.g.Hydrochloric Acid, Nitric Acid and Sulfuric Acid used for biodiesel production and its productivity is measured. The optimum combination for Each Acid catalyst is established. So the three Bio-diesels are produced for each acid catalyst.

B. Pretreatment of oil for biodiesel production:

Initially the oil is filtered though strainers to remove any impurities, foreign partical and solid debris present in it. The filtered oil is heated above 100^0c for 30 to 40 min to remove any water contents in it and it also improves the reactivity of oil. As per literature review, the water content should not be more than 0.04%(wt %). Higher water contents are not good for Biodiesel production via acid catalysis.

C. *NA-O-CH_3 preparation for biodiesel production*:

Initially the Methanol is dries by Silica Granule and finally it is then deepfreeze. Analytical Reagent (AR) quality potassium hydroxide surface is cleaned by steel knife and its weight is measured quickly. Then Potassium Hydroxide (KOH) is mixed with methanol in the beaker .The magnetic rotor machine (MRM) is used to completely dissolve the Potassium Hydroxide (KOH) in methanol to produce NA-O-CH_3.The complete solution is stirred from 15 min to 20 min to get homogeneous solution.

D. Systematic Procedure (i.e. Protocol) for process of Biodiesel Production

-In the begaining the wastecookingoil (WCO) isheated at 60^0 C which in termsimproves the reactivity of oil.

-The pretrement of obtainedoilisperformed by treatingitwithany of the strongacid e.g. HCL,HNO3,H2SO4 to reduce Free Fatty Acid (FFA) .The pretreatedoilisthenheated in water bath at constant temperature of 70^0 C for 60 minutes. The solution isstirredvigourslywhileheating.

- The PH of oilischecked by PH analyser whichshould lie between 6 to 7. If PH is not between permissible limitthen time of heatingisextended.
- TAN Count of Pretretedoilismeasured by dissolving KOH in it. TAN count shouldbelessthan 1 mg/ gm of pretreatedoil.
- FFA isremoved by the centrifuging machine. The centrifuging machine isoperated on optimum conditions at 5200 RPM for 20 Minutes.

The Centrifuging machine isused to remove the FFA fromrawoil. The centifuging machine isoperated at 5200 RPM for 20 Minutes. The FFA separated at upper portion and oilisremained at the bottomwhichcanbeeasialyremoved.

-NAOH is mixed withmethanol in amagnetic rotor machine and stirred for some time to prepare sodium methoxide solution. Magnetic Rotor Machine (MRM) used to prepare sodium methoxide solution in which the beakerisplaced on magneticfieldplatform. The rotor whichisnothing but the magnetsisdipped in beaker. The MRM fréquently changes magneticfield and rotor responds i.e. rotatesaccordingly and rotory motion is setups.

-The produced sodium methoxide (Na-O-CH3) solution istreatedwithaboveproducedoilwhichishavingless FFA content at a constant temperature of 60^0 C.

The biodiesel formation startsfrom 20 min onword. The biodiesel samplefrequentlyextractfromevery five minutes to analyse the quality to meet ASTM fuel requirement. The selection of best sampleisdoneimperically.

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-Glycerinisremoved by centrifuging Machine.

-Theseprocedureisfollwed for eachacidHydrocloric Acid, Nitric Acid And Sulfuric Acid.

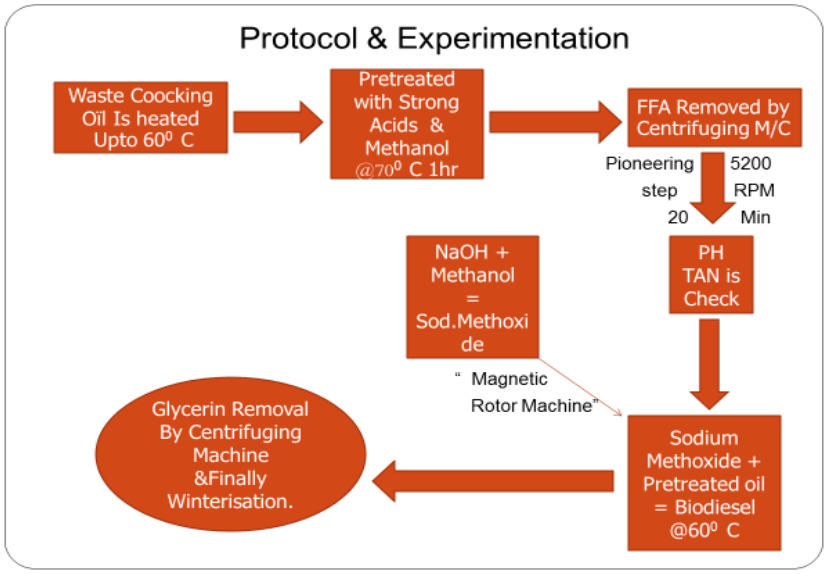

Fig.1.Complete Procedure for biodiesel production

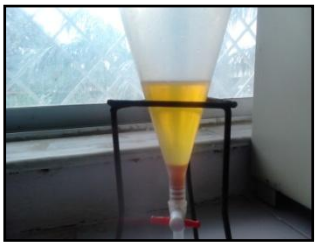

Fig.2.Waste Cooking oil (WCO)Fig .3. Biodiesel Produced from Waste Cocking oil

IV EXPERIMENTATIONS & RESULTS

Table I: Chemical combination for Biodiesel production using HCL, HNO3 & H2SO4

S. N.	Methanol/Pretreated oil	Acid Concentration	Temp (^{0}C)	Time	Yield (%)	Glycerin (Wt)	Viscosity Astm 1.9-6.0	CV	Flash point	Fire point	TAN	Results
HCL												
1	0.12	0.75%	60	35	20	21.67	7.11	40525	135	141	0.2922	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**	5.78	40312	130	137	0.3585	BD form after 20 min and mostly acceptable upto40 after more viscous BD form.
3	0.20	1.25%	60	51	61.6	8.11	9.54	38522	142	148	0.3736	BD form in some minutes but unacceptable & heating time hence Increased which results into viscous formations.
4	0.24	1.50%	60	60	28.48	19.96	10.45	36155	157	163	0.4189	BD form in some minutes but viscous and unacceptable.
5	0.28	1.75%	60	69	52.8	14.62	12.33	36555	168	175	0.4324	BD form in some minutes but viscous and unacceptable.
HNO3												
6	0.12	0.75%	60	90	79.33	15.48	3.98	39256	142	148	0.4072	BD Form after 70 min less viscous but not meet ASTM .
7	0.16	1%	60	55	81.06	12.76	4.12	38912	145	151	0.4398	BD Form after 55 min less viscous but not meet ASTM.
8	**0.20**	**1.25%**	**60**	**60**	**92.734**	**8.89**	4.99	38522	135	142	0.4512	BD Form after 40 min less viscous And meets ASTM.
9	0.24	1.50%	60	75	50.63	26.142	5.98	36155	171	180	0.5986	BD Form after 20 min more viscous.
10	0.28	1.75%	60	80	40.07	31.39	6.33	36555	173	181	0.6123	BD Form emidiadtly but more viscous.
H2SO4												
11	0.12	1%	60	45	90.848	18.60	5.68	36536	134	140	0.3024	BD Form after 20 min but poor qualupto 40Above good upto 90 min and then viscous.
12	0.16	1.25%	60	40	94.723	14.36	6.25	38988	125	131	0.3235	BD Form after 15 min but poor quality.
13	**0.20**	**1.50%**	**60**	**24**	**99.009**	**11.58**	5.20	409100	120	126	0.3350	BD form emidiatly after 40 min visco increases drastically.
14	0.24	1.75%	60	65	95.0628	13.92	6.11	39889	171	178	0.3581	BD form immediately but unacceptable.
15	0.28	2.00	60	88	98.174	12.36	7.14	37566	169	176	0.3815	BD form immediately but unacceptable.

Biodiesel produced via different Acids

A. **Biodiesel Production via hydrochloric Acid**

When Hydrochloric acid (HCL) used for pretreatment of WCO to produce biodiesel.Empirical performances of biodiesel production via.Hydrocloric acid depicts that biodiesel production starts after 25 min and continues heating after 45 min leads to production of unacceptable biodiesel.The best optimum combinations is Acid concentration, Methanol/pretreated oil and time wise is 1%, 0.16 and 28 min gives highest yield more than 81 %. The biodiesel produced at this optimum stage meets ASTM fuel requirement.Fig 4 shows the optimum combination while Fig.5.shows the Solid & Glycerin (Wt%) of Biodiesel process.

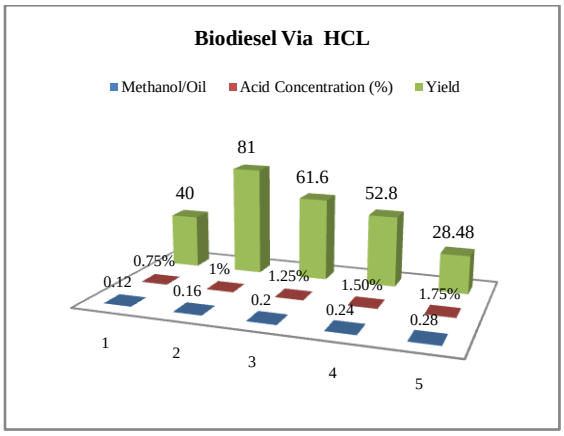

Fig.4.Biodiesel Processes Via HCL

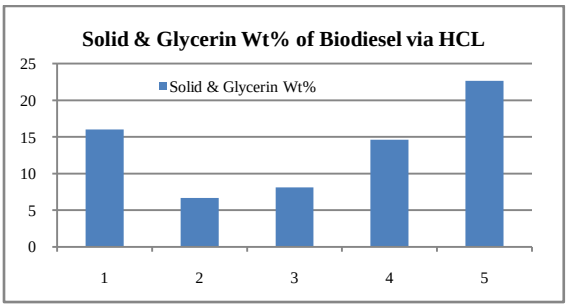

Fig.5. Solid &Glycerin (Wt%) of Biodiesel Processes Via HCL

B. Biodiesel Production via Nitric Acid

When Nitricacid (HNO_3) used for pretreatment of WCO to produce biodiesel.Empirical performances of biodiesel production via.Nitric acid depicts that biodiesel production starts after 40 min.

The best optimum combinations is Acid concentration, Methanol/pretreated oil and time wise is 1.25%, 0.20 and 50 min gives highest yield more than 92.734 %. The biodiesel produced at this optimum stage meets ASTM fuel requirement.

Fig.6. shows the optimum combination while Fig.7.shows the Solid & Glycerin (Wt %) of Biodiesel process. Figures conclude that the combination '3' gives High yield with Low solid & glycerin formation.

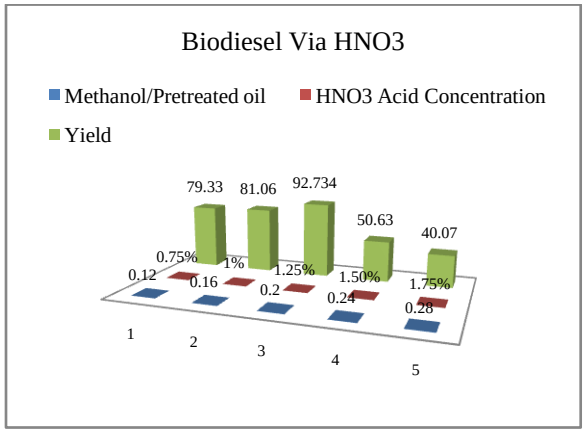

Fig.6. Biodiesel Processes Via HNO_3

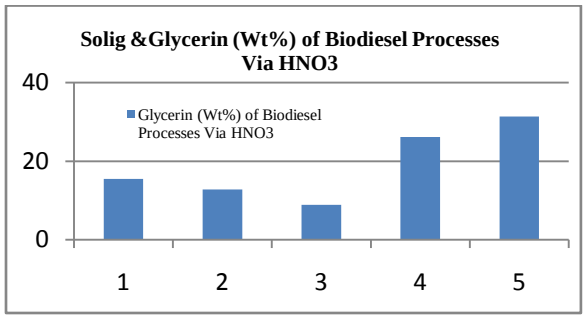

Fig.7. Glycerin (Wt%) of Biodiesel Processes Via HNO_3

C. Biodiesel Production via Sulfuric Acid

When sulfuric acid (H_2SO_4) used for pretreatment of WCO to produce biodiesel.Empirical performances of biodiesel production via.Sulfuric acid depicts that biodiesel production starts after 25 min and continues heating after 45 min leads to production of unacceptable biodiesel. The best optimum combinations is Acid concentration, Methanol/pretreated oil and time wise is 1.5%, 0.2 and 24 min gives highest yield more than 99.009 %. The biodiesel produced at this optimum stage meets highest ASTM fuel requirement.

Fig.8. shows the optimum combination while Fig.9. shows the Solid &Glycerin (Wt %) of Biodiesel process.Figures conclude that the combination '3' gives High yield with Low glycerin formation.

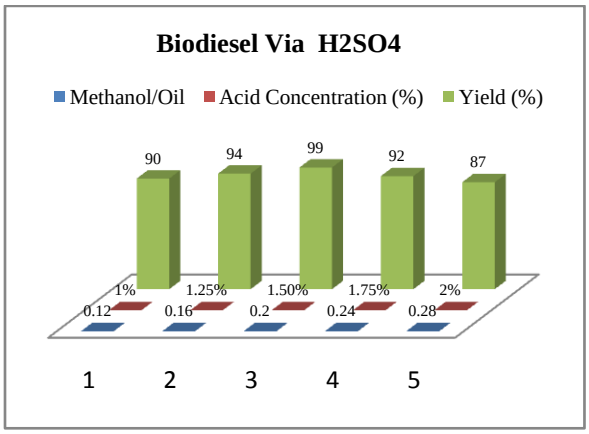

Fig.8. Biodiesel Processes Via H_2SO_4

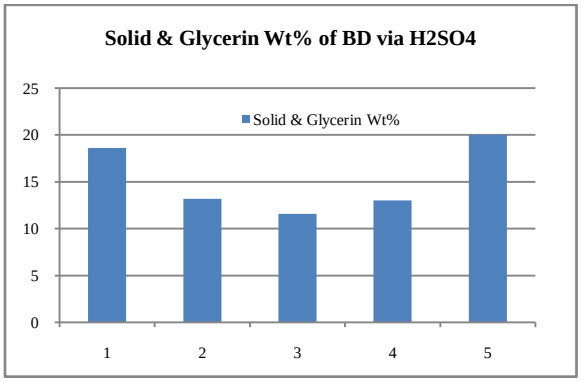

Fig.9. Glycerin (Wt%) of Biodiesel Processes Via H_2SO_4

D. Biodiesel ProductionComparison for different Acids.

The best optimum combination of biodiesel production is via Sulfuric acid which gives highest

yield than other acids. The biodiesel produced via $H_2SO_4$is of best quality. The biodiesel produced by using HCL not only gives better results but also of better properties

V. CONCLUSIONS

Biodiesel is a potential substitute for petro-diesel fuels. The benefits of biodiesel are the enhance lubricity, lower emission and reduced global warming gases. Biodiesel from waste cocking oil has potential as an alternative energy source.However, this oil alone will not solve our dependence on foreign oil within any practical time frame. Use of this withother alternative energy sources and suitable additives could contribute to a more stable supply of energy. Biodieselthus produced meets the standard biodiesel specifications. The production and consumption of biodiesel will inevitablyrise in future due to low environmental impact, ease of handling, and possibility of use without need for majoradjustments of existing engines of motor vehicles.

Biodiesel Optimum Combinations

1) The best optimum combinations of biodiesel produced using Hydrocloric Acid is Acid concentration, Methanol/pretreated oil and time wise is 1%, 0.16 and 28 min gives highest yield more than 81 % which is of ASTM Fuel quality.
2) The best optimum combinations of biodiesel produced using Nitric Acid is Acid concentration, Methanol/pretreated oil and time wise is 1.25%, 0.20 and 50 min gives highest yield more than 92.734 % which is of ASTM Fuel quality.
3) The best optimum combinations of biodiesel produced using sulfuric Acids Acid concentration, Methanol/pretreated oil and time wise is 1.5%, 0.2 and 24 min gives highest yield more than 99.009 % which is of ASTM Fuel quality.
4) The yield of biodiesel production is obtained highest by sulfuric acid, moderatein case of nitric acid and lowest in case of hydrocloric acid but the biodiesel produced via HCL shows good fuel properties than nitric Acid
5) Winterization and other processes to improve cold storage propertyand reduce ignition delay.

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