

**STUDY OF ADDITIVE RESPONSE ON
RHEOLOGICAL PROPERTIES (CLOUD POINT/POUR
POINT) OF BIODIESEL**

A PROJECT REPORT

**SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF**

MASTER OF TECHNOLOGY

IN

Refining & Petrochemical Engineering

(Academic year: 2005-2007)

BY

B. CHANDRAGUPTHAN

R.080205005

Under the guidance of

Internal Guide

Dr. D. N. Saraf

Distinguished Professor

College of Engineering

U.P.E.S

Dehradun

External Guide

Dr. Savita Kaul

Scientist 'E-1'

CSD Division

IIP

Dehradun

UPES - Library

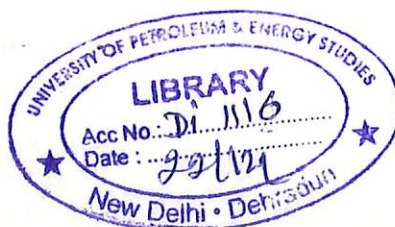


D11116

CHA-2007MT



College of Engineering
University of Petroleum and Energy Studies
May 2007



ACKNOWLEDGEMENT

I would like to thank **Dr.M.O.Garg, Director, Indian Institute of Petroleum** for giving me the opportunity to work on this project. I wish to endorse my sincere gratitude and cordial thanks to **Dr. Savita Kaul, Scientist 'E-I', CSD Division, Indian Institute of Petroleum, Dehradun** for her encouraging attitude, expert advice and guidance through out my training.

I wish to express my appreciation and cordial thanks to **Dr. D.N. Saraf, Distinguished Professor, University of Petroleum & Energy Studies**, for making provisions, encouraging and guiding me for my major project, which has been of inestimable value in my pursuit of achieving the Masters in Refining & Petrochemical Engineering from University of Petroleum and Energy Studies, Dehradun.

To **Dr. B.P. Pandey, Dean, UPES, Dehradun**. I owe more than can be expressed for his kind supervision, special interest, ceaseless help and valuable suggestion during my training with Indian Institute of Petroleum.

I would like to thanks **DR. R. P. Badoni** for his Kind assistance and guidance throughout my training.

Thanks to all those who directly or indirectly contributed to for my training at Indian Institute of Petroleum and UPES.

B. Chandragupthan



भारतीय पेट्रोलियम संस्थान

वैज्ञानिक तथा औद्योगिक अनुसंधान परिषद्
हरिद्वार रोड, मोहकम्पुर
देहरादून-२४८००५, उत्तरांचल, भारत

INDIAN INSTITUTE OF PETROLEUM

(Council of Scientific & Industrial Research)

Haridwar Road, Mohkampur,

Dehradun-248 005, Uttaranchal, India



Creating Future Fuels

May 4, 2007

CERTIFICATE

This is to certify that the Project entitled “**Study of Additive Response on (Cloud point/Pour point) Rheological Properties of Biodiesel**” being submitted by B. Chandraguptan, for the partial fulfillment of M.Tech. (RPCE) degree to UPES, Dehradun is a bonafide work carried by him under my guidance and supervision at the **Indian Institute of Petroleum (IIP)** from 5th March to 1st may 2007. During the course of his training I found him possessing outstanding ability to grasp new concepts. He also exhibited excellent logic development skills in all his assignments.

I wish him success in all his future academic endeavours.

S. Kaul
4/5/07

(Dr. Savita Kaul)

Scientist E-I

Chemical Sciences Division



UNIVERSITY OF PETROLEUM & ENERGY STUDIES

CERTIFICATE

This is to certify that the project work entitled “**Study of additive response on Rheological properties (cloud point/pour point) of Bio diesel**” submitted by B. Chandragupthan M.Tech (Refining & Petrochemical Engineering), University of Petroleum and Energy Studies, Dehradun under our guidance of Dr. D. N. Saraf, Distinguished Professor, College of Engineering, UPES and Dr. Savita Kaul, Scientist ‘E-1’, CSD division, IIP, Dehradun in the partial fulfillment for the degree of Master of Technology in Refining & Petrochemical Engineering. No part of this project has been submitted else where for any other degree.

Dr D. N. Saraf

Distinguished professor, COE

University of Petroleum & Energy Studies

Dehradun

Corporate Office

Hydrocarbons Education & Research Society
1st Floor, PHD House, 4/2, Siri Institutional Area
August Kranti Marg, New Delhi-11001 India
Ph. : +91-11-41730151-53 Fax : +91-11 1730154

Main Campus :

Energy Acres, PO Bidholi, Via Prem Nagar,
Dehradun-248 007 (Uttarakhand) India
Ph. : +91-135-2261090-91, 2694201/203/208
Fax : +91-135-2694204

Regional Centre (NCR)

SCO 9-12, Sector 14, Gurgaon 122 007
(Haryana), India
Ph : +91-124-4540300
Fax : +91 124 4540 330




UNIVERSITY OF PETROLEUM & ENERGY STUDIES

CERTIFICATE

This is to certify that the project work entitled “Study of additive response on Rheological properties (cloud point/pour point) of Bio diesel” submitted by B. Chandragupthan in partial fulfillment of the requirements for the award of the degree of Master Of Technology (Refining & Petrochemical Engineering), at college of engineering, University of Petroleum and Energy Studies, is a record of the work carried by him at Indian Institute of Petroleum under the guidance of Dr. D. N. Saraf, Distinguished Professor, COE, UPES and Dr. Savita Kaul, Scientist ‘E-1’, CSD division. IIP, Dehradun.

To the best of my knowledge, the contents of this project work did not form a basis of the award of any previous degree or published material by any one else.

The work is comprehensive of sufficient standard and here by recommended for the award of M. Tech in Refining & Petrochemical Engineering.


11.01.07


Dr. D. N. Saraf

Distinguished professor,

COE

U.P.E.S

Dehradun


22.01.07

Dr. B. P. Pandey

Dean,

COE

U.P.E.S

Dehradun

Corporate Office

Hydrocarbons Education & Research Society
1st Floor, PHD House, 4/2, Siri Institutional Area
August Kranti Marg, New Delhi-11001 India
Ph. : +91-11-41730151-53 Fax : +91-11 1730154

Main Campus :

Energy Acres, PO Bidholi, Via Prem Nagar,
Dehradun-248 007 (Uttarakhand) India
Ph. : +91-135-2261090-91, 2694201/203/208
Fax : +91-135-2694204

Regional Centre (NCR)

SCO 9-12, Sector 14, Gurgaon 122 007
(Haryana), India
Ph : +91-124-4540300
Fax : +91 124 4540 330

ABSTRACT

Bio diesel is the name applied to the renewable fuels manufactured by the trans- esterification of vegetable oils or animal fats which can be used as a substitute for or as an additive to mineral diesel. There has been a considerable interest in developing bio-diesel as an alternative fuel in recent years due to its environmental benefits and because it is derived from renewable resource like vegetable oils or animal fats. However, the freezing and gelling of many bio-diesel formulations are limiting their applications.

Cloud point at which crystallization begins, cold filter plugging point at which fuel start to plug a fuel filter, and pour point at which fuel no longer pours. In this work the additive response on (cloud point and pour point) rheological properties of bio-diesel were studied.

TABLE OF CONTENTS

CHAPTER No	NAME	Pg. No
1	INTRODUCTION	1-3
2	LITERATURE REVIEW	4-6
3	BIODIESEL STANDARDS	7-21
4	STRATEGIES	22-24
5	EXPERIMENTAL RESULTS	25-34
	DISCUSSION	
6	BIBLIOGRAPHY	35-36

CHAPTER 1

INTRODUCTION

Any fuel derived from biomass is known generically as bio-fuels. Biodiesel is a partial replacement for petroleum diesel that is non toxic, bio degradable, and sustainable. It is made through a chemical process called trans-esterfication, which produces two valuable products-FAME and glycerin, which finds applications in soap making and other products. The process can be carried out in the presence of both the homogeneous and heterogeous catalyts. Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable lipid sources.

HISTORY

The concept of using vegetable oil based fuel dates back to 1895 when Dr. Rudolf developed the first compression engine to specifically run on peanut oil, as he demonstrated at the world exhibition in Paris in 1900. Castor oil was used in the diesel engine in Argentina in 1916. Shay stated the use of palm oil as a diesel fuel as early as 1920. During world war II, both the allies and NAZI Germany utilize bio-mass fuel in their machines. However the increased availability and low cost of petroleum derived diesel fuel caused the use of renewable fuels to fade.

CHEMISTRY OF BIODIESEL

All vegetable oil and animal fats primarily considered as triglycerides because they are ester made up of three fatty acids joined to a glycerol molecule. Transesterfication is a process of displacement of an alcohol group from an ester by another alcohol. The nature of the fatty acid components of glycerides plays an important role in determining the physico-chemical properties of bio-oil. In the process of trans-esterfication of bio-oil, in particular the glyceride, an alcohol is used to replace the Glycerine to obtain ester of fatty acids, however, with lower molecular weight.

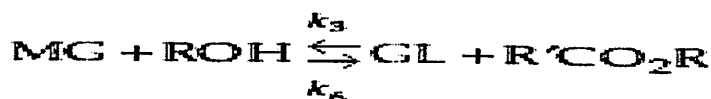
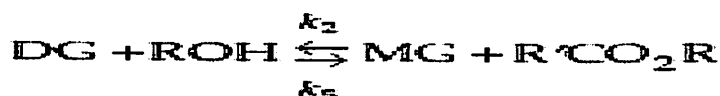
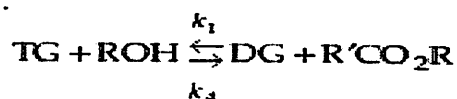
The reaction can be catalyzed by alkalies, acid or enzymes. Alkali-catalyzed transesterfication is much faster than acid catalyts, but it is not suitable for esterfication of free fatty acids. Because, alkaline catalyts are very sensitive to free fatty acids. During the reaction, free fatty acids may react with an alkali catalyts to form soap and water, which diminishes the ester yield. Therefore acid catalyts such

as H₂SO₄ and HCl are preferred for esterification of free fatty acids. In addition, acid-catalyzed esterification reaction of free fatty acids is relatively faster than acid-catalyzed transesterification reaction of triglycerides. (Ali Keskin et al ¹)

The thermal transesterification reaction can be considered in the following way. Triglyceride (TG) reacts with methanol to produce diglyceride (DG) which further reacts with methanol to produce monoglyceride (MG). Finally, monoglyceride reacts with methanol to give glycerol. At each reaction step, one molecule of methyl ester is produced for each molecule of methanol consumed. This kinetic mechanism can be represented by the following reactions:



The stepwise reactions are:



Each reaction step is assumed to be of first order with respect to each reacting component and irreversible. Transesterification reactions are in principle equilibrium reactions, but pilot experiments have shown that at the conditions at which the experiments of this work were carried out the reverse reactions are not important and do not influence the forward reaction rates. This is mainly attributed to the high methanol content used in the thermal transesterification experiments.

GLOBAL SCENARIO

Global demand for bio diesel is expected to increase from 6.9 million tons in 2006, to 44.8 million tons in 2010, according to a study published last year by SRI consulting (SRIC; MENLO PARK, CA).Asia is expected to overtake North America and Central and Eastern Europe to become the second biggest regional producer of Bio diesel after Western Europe by 2010, SRIC says.

Germany is currently the world's leading producer of Bio diesel, with a production of 2 billion litres / year for domestic consumption. Brazilian government expects that by 2007 the country will be able to produce Biodiesel at 1.2 Billion liter/year. Japanese government had earlier introduced a crash program to build 11 Bio diesel plants, with production targets of 187 million liters in 2007 and 1.3 billion liters by 2010, or equivalent to 3% of that country's total fuel consumption.

CHAPTER 2

LITERATURE REVIEW

Hiroaki Imahara et al² (2006) observed a drastic increase in cloud point when the total amount of saturated esters increased. Cloud point depends mostly on the saturated ester content and the effect of unsaturated ester composition can be negligible. On the other hand, high unsaturation of fatty acid methyl esters causes polymerization and oxidation of the fuel.

Chuang-Wei Chiu et al³ (2004), In diesel fuels, a few polymer additives having long hydrocarbon chains have been observed to delay observable crystal formation as a petroleum diesel is cooled. These additives tend to reduce the visibility of the crystals and not their formation. Many additives contain proprietary components and copolymers of ethylene and vinyl acetate or other olefin-ester copolymers.

Similar approaches will be considerably more challenging to develop an additive for biodiesel blends because biodiesel has less chemical diversity. Biodiesel is comprised of fewer chemical components present in higher composition than petroleum diesel. The lack of chemical diversity in biodiesel fuels narrows the temperature gap between the cloud point and pour point.

Most additives function by crystal modification, reducing the size and shape of the wax crystals. Hence, they do not generally affect the cloud point. They inhibit the crystals from growing to a size large enough to plug filters and provide a barrier to crystal agglomeration.

Metin guru et al¹ (2007) observed that, the resinic acids were reacted with MnO₂ and NiO in order to produce metallic based fuel additives, which is dosed in to blend fuels, they found

- No significant different in the engine torque, power output
- Specific consumption increases (Because of low caloric value of biodiesel)
- Mn and Ni based metallic additives reduced the pour point and the viscosity of the biodiesel fuels
- But NO_x emission is high. The higher NO_x value is probably because of the Mn additives having more catalyst effect on composition causing to increase the maximum temperature

Hiroaki Imahara et al ² (2006) observed that, the saturated esters, which have higher cloud point than unsaturated ones, have a significant effect on characterizing its cold properties.

Nestor.Soriamo. Jr et al ⁴ (2006) demonstrated that the use of secondary alcohols such as isopropanol or 2-Butanol instead of methanol leads to product of lower pour point .However ,the use of branched chain alcohol increases the viscosity of the product due to the presence of relatively higher amount of mono and di glycerides as a result of incomplete transesterfication.This was attributed to the lesser nucleophilicity and greater steric hindrance of the alkyl groups adjacent to the carbon atom bearing the –OH of the secondary alcohols.

Molecular structure of pour point depressants for conventional diesel fuel is composed of polymeric hydrocarbon chain with protruding polar groups. Their most widely accepted mechanisms of action include adsorption, co-crystallization, nucleation and improved wax solubility. It is very likely that vegetable oil and their corresponding FAME have strong interaction at low temperature. However; vegetable oil lacks polar groups, which has to be introduced in its structure to make it an effective pour point depressant.

Pour point and cloud point were the most affected by the presence of unsaturation. All of these properties are believed to be affected by the intermolecular forces of attraction, which becomes greater with increasing chain length. The presence of double bonds disrupts the attractive forces operating between molecules along the hydrocarbon chain and hence causing these physical properties to decrease.

The higher the proportion of saturated components therefore leads to higher cloud point and pour point. The cis double bonds in unsaturated components hampered crystal packing thus resulting in lower pour point.

Studies showed that ozonation of neat SFO gives 90% ozonide with 1,2,4-trioxolane rings with fatty acid moieties whose chain lengths are similar to the corresponding FAME components of biodiesel and with the presence of 1,2,4-trioxolane polar rings in the fatty acid chains, ozonized vegetable oils therefore are potential pour point depressants for biodiesel.

The similarities in the chemical structure of the components of biodiesel and the additives make their interaction in the solid phase greater, leading to a lower pour point. Pour point depressants best when the average lengths of its hydrocarbon chain is the same as that of the main components of the materials being treated because of the strong intermolecular force of attraction operating along their hydrocarbon chains.

The most significant reduction in pour point was observed when the biodiesel and additive were prepared from the same vegetable oil

Microscopic analysis revealed that ozonized vegetable oils prevent the agglomeration of crystals that resulted in the formation of smaller and more regular shaped solids, thus maintaining the fluid flow properties of the biodiesel.

Jatropha Bio-diesel has poor oxidation stability with good low temperature properties. On the other hand, palm Bio-diesel has good oxidation stability, but poor low temperature properties. Therefore, optimum mixture of Jatropha Bio-diesel can lead to a synergistic combination which improves oxidation stability and low temperature property.

Rakesh sarin et al⁵ reported that, Jatropha-palm (60:40) blend was tested for low temperature properties and found to exhibit cloud point of 10⁰C and CFPP of 5⁰C. Thus, then blending of palm Bio-diesel in Jatropha Bio-diesel exhibits additive response in cloud and pour point properties.

CHAPTER 3

BIODIESEL STANDARDS

EUROPEAN STANDARD (EN14214): (Bredakegel et al ⁶)

Cetane No.	= > 51
Ester content (% m/m)	= > 96.5
Sulfur content (mg/kg)	= < 10
Carbon residue on 10%	= < 0.3
Distillation residue (%m/m)	= < 0.3
Water content (mg/kg)	= < 500
Oxidation stability	= > 6
Acid value (mg of KOH/gm)	= < 0.50
Iodine Value (gm of I ₂ /100 gm)	= < 120
Linolenic acid methyl ester (%m/m)	= < 12
Methanol content (% m/m)	= < 0.20

ASTM D6751: (P.P.Bhojvaid et al ⁷)

Flash point (closed cup) - D93	= 130 ⁰ C (min)
Water or Sediment Vol- D 2709	= 0.050 % (max)
Kinematic Viscosity @ 40 ⁰ C – D445	= 1.9-6 mm ² /sec
Sulphated ash – D874	= 0.020 % mass (max)
Suphur – D5453	= 500 ppm (max)
Copper strip corrosion – D130	= No: 3 (max)\
Cetane No. – D613	= 47 (min)
Cloud Point – D2500	= Report
Carbon Residue – D4530	= 0.050% mass (max)
Acid No – D664	= 0.80 mg KOH/gm (max)
Free Glycerine – D6584	= 0.020 % mass
Total Glycerine – D6584	= 0.240 % mass
Phosphate content-D4951	= 0.001 % mass (max)
Distillation Temp.AET, - D1160	= 360 ⁰ C ,max
90 % recovered (AET-Atmospheric Equivalent Temperature)	

PROPOSED INDIAN STANDARD:

Density at 15 ⁰ C, kg/m ³	= 860-900
Kinematic Viscosity at 40 ⁰ C cSt	= 2.5-6
Flash point (PMCC) ⁰ C, min	= 120
Sulphur, mg/kg max.	= 50
Carbon residue (Ramsbottom), % by mass, max	= 0.05
Sulfated ash, % by mass, max	= 0.02
Water content, Mg/kg, max	= 500
Total contamination mg/kg, max	=24
Cu corrosion, 3 hrs at 50 ⁰ C, max	= 1
Cetane No., min	=51
Acid value, mg KOH/g.max	=0.50
Methanol@, % by mass, max	=0.20
Ethanol, @% by mass, max	=0.20
Ester content, %by mass, min	=96.5
Free Glycerol, % by mass, max	=0.02
Total Glycerol, % by mass, max	=0.25
Phosphorous, mg/kg, max	=10
Sodium and potassium, mg/kg max	= To report
Calcium and Magnesium, mg/kg max	= To report
Oxidation stability, at 110 ⁰ C, hrs, min	= 6

COLD FLOW PROPERTIES

- **Freezing Point:** It is the temperature at which crystals of hydrocarbons formed on cooling and disappear when temperature of fuel is allowed to rise.
- **Cloud Point and Pour Point:** Cloud Point is the temperature at which a cloud or haze of wax crystals appears at the bottom of the test jar when the oil is cooling under prescribed conditions.
- Pour Point is well established test to estimate the temperature at which a sample of oil becomes sufficiently solid to prevent its movement by pumping. It indicates the waxy nature of the oils.
- Cloud Point gives a rough idea of the temperature above which the oil can be safely handled without any fear of congealing or filter clogging.
- The cold filter plugging point test is used to determine the extent to which diesel fuel or gas oil will flow, even though the temperature is below that at which wax crystals normally appear .i.e., cloud point.

STANDARD TEST METHOD FOR CLOUD POINT

Scope

This test method covers only petroleum products and bio-diesel fuels that are transparent in layers 40 mm in thickness, and with a cloud point below 49°C.

Summary of Test Method

The specimen is cooled at a specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded as the cloud point.

Significance and Use

For petroleum products and biodiesel fuels, cloud point of a petroleum product is an index of the lowest temperature of their utility for certain applications.

Apparatus

Test Jar, clear, cylindrical glass, flat bottom, 33.2 to 34.8-mm outside diameter and 115 and 125-mm height. The inside diameter of the jar may range from 30 to 32.4 mm within the constraint that the wall thickness be no greater than 1.6 mm. The jar should be marked with a line to indicate sample height 54 ± 3 mm above the inside bottom.

- 1) Cork, to fit the test jar, bored centrally for the test thermometer.
- 2) Jacket, metal or glass, watertight, cylindrical, flat bottom, about 115 mm in depth, with an inside diameter of 44.2 to 45.8 mm. It shall be supported free of excessive vibration and firmly in a vertical position in the cooling bath so that not more than 25 mm projects out of the cooling medium.
- 3) Gasket, ring form, about 5 mm in thickness, to fit snugly around the outside of the test jar and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test jar and hard enough to hold its shape. Its purpose is to prevent the test jar from touching the jacket.

- 4) Bath or Baths, maintained at prescribed temperatures with a firm support to hold the jacket vertical. The required bath temperatures may be maintained by refrigeration if available, otherwise by suitable freezing mixtures.

The mixtures commonly used for temperatures down to those shown are as follows:

- 1) Ice and water 10°C
- 2) Crushed ice and sodium chloride crystals - 12°C
- 3) Crushed ice and calcium chloride crystals - 26°C
- 4) Acetone, methyl or ethyl alcohol, or petroleum naphtha chilled in a covered metal beaker with an ice-salt mixture to - 12°C, then with enough solid carbon dioxide to give the desired temperature - 57°C.

Reagents and Materials

Acetone—Technical grade acetone is suitable for the cooling bath, provided it does not leave a residue on drying. (**Warning**—extremely flammable.)

Calcium Chloride—Commercial or technical grade calcium chloride is suitable.

Carbon Dioxide (Solid) or Dry Ice—A commercial grade of dry ice is suitable for use in the cooling bath.

Ethanol or Ethyl Alcohol— A commercial or technical grade of dry ethanol is suitable for the cooling bath. (**Warning**—Flammable. Denatured, cannot be made nontoxic.)

Methanol or Methyl Alcohol—A commercial or technical grade of dry methanol is suitable for the cooling bath. (**Warning**—Flammable. Vapor harmful.)

Petroleum Naphtha—A commercial or technical grade of petroleum naphtha is suitable for the cooling bath. (**Warning**—Combustible. Vapor harmful.)

Sodium Chloride Crystals—Commercial or technical grade sodium chloride is suitable.

Sodium Sulfate—A reagent grade of anhydrous sodium sulfate should be used when required.

Procedure

1) Bring the sample to be tested to a temperature at least 14°C above the expected cloud point. Remove any moisture present by a method such as filtration through dry lintless filter paper until the oil is perfectly clear, but make such filtration at a temperature of at least 14°C above the approximate cloud point.

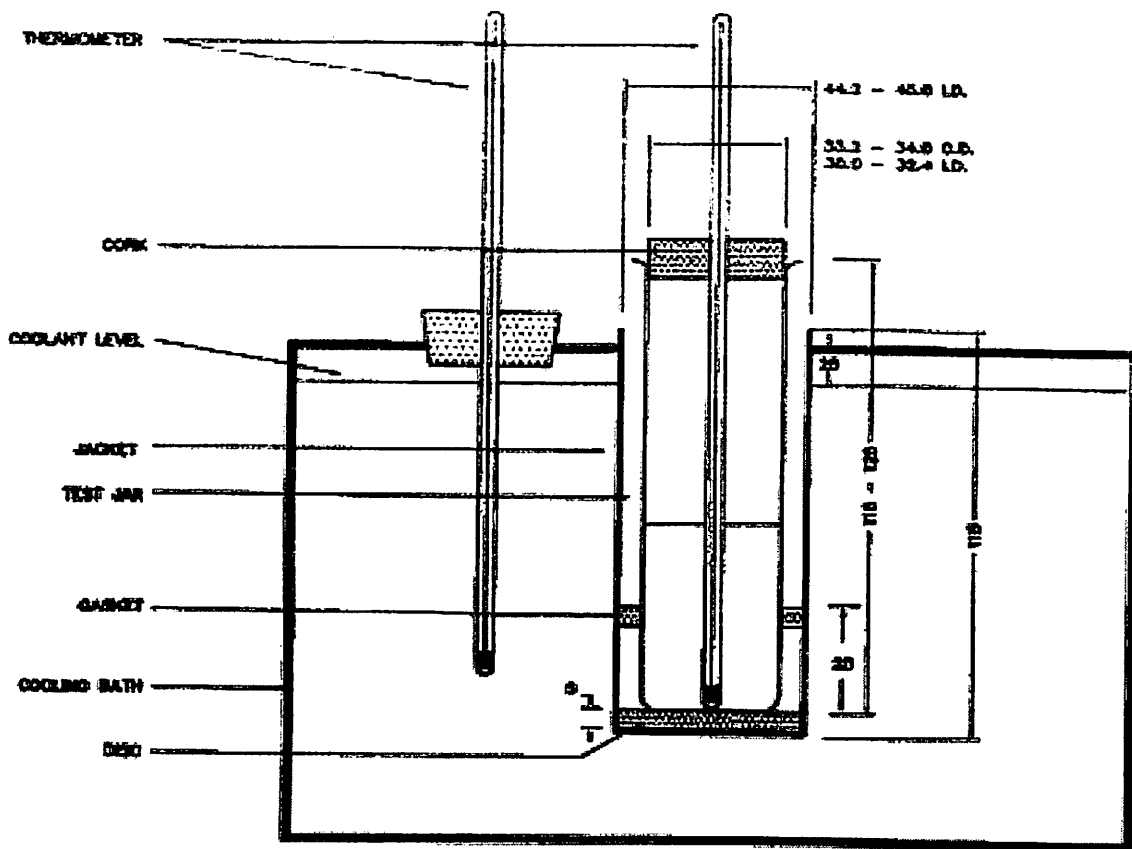
2) Pour the sample into the test jar to the level mark.

3) Close the test jar tightly by the cork carrying the test thermometer. Use the high cloud and pour thermometer if the expected cloud point is above - 36°C and the low cloud and pour thermometer if the expected cloud point is below - 36°C Adjust the position of the cork and the thermometer so that the cork fits tightly, the thermometer and the jar are coaxial, and the thermometer bulb is resting on the bottom of the jar.

4) See that the disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. The disk and jacket shall have been placed in the cooling medium a minimum of 10 min before the test jar is inserted. The use of a jacket cover while the empty jacket is cooling is permitted. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium. Failure to keep the disk, gasket, and the inside of the jacket clean and dry may lead to frost formation, which may cause erroneous results.

5) Maintain the temperature of the cooling bath at 0 to 1.5°C.

6) At each test thermometer reading that is a multiple of 1°C, remove the test jar from the jacket quickly but without disturbing the specimen, inspect for cloud, and replace in the jacket. This complete operation shall require not more than 3 s. If the oil does not show a cloud when it has been cooled to 9°C, transfer the test jar to a jacket in a second bath maintained at a temperature of - 18°C \pm 1.5°C (see Table 1).



NOTE—All dimensions are in millimetres.
FIG. 1 Apparatus for Cloud Point Test

Do not transfer the jacket. If the specimen does not show a cloud when it has been cooled to -6°C , transfer the test jar to a jacket in a third bath maintained at a temperature of -33°C . For the determination of very low cloud points, additional baths are required, each bath to be maintained in accordance with Table 1. In each case, transfer the jar to the next bath, if the specimen does not exhibit cloud point and the temperature of the specimen reaches the lowest specimen temperature in the range identified for the current bath in use, based on the ranges stated in Table 1.

TABLE 1 Bath and Sample Temperature Ranges

Bath	Bath Temperature Setting, $^{\circ}\text{C}$	Sample Temperature Range, $^{\circ}\text{C}$
1	0 ± 1.5	Start to 9^{\dagger}
2	-18 ± 1.5	9 to -8
3	-33 ± 1.5	-8 to -24
4	-51 ± 1.5	-24 to -42
5	-69 ± 1.5	-42 to -80

7) Report the cloud point, to the nearest 1°C, at which any cloud is observed at the bottom of the test jar, which is confirmed by continued cooling. A wax cloud or haze is always noted first at the bottom of the test jar where the temperature is lowest. A slight haze throughout the entire sample, which slowly becomes more apparent as the temperature is lowered, is usually due to traces of water in the oil. Generally this water haze will not interfere with the determination of the wax cloud point. However, if the haze is very dense, a fresh portion of the sample should be dried by shaking 100 mL with 5 g of anhydrous sodium sulfate for at least 5 min and then filtering through dry lintless filter paper. Given sufficient contact time, this procedure will remove or sufficiently reduce the water haze so that the wax cloud can be readily discerned. Drying and filtering should be done always at a temperature at least 14°C above the approximate cloud point but otherwise not in excess of 49°C.

Precision

The precision of this test method as determined by statistical examination of inter laboratory results is as follows.

Repeatability

The difference between two test results obtained by the same operator, using the same apparatus, under constant operating conditions, on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 2°C only for distillate products and 6°C for other products only one in case in 20.

Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 4°C only for distillate products and 6°C for other products only one in case in 20.

Test Report

The test Report shall contain at least the following information

- a) All details necessary to identify the product tested.
- b) The result of the test.
- c) The date of the test. (Jhon Phipps⁸)

STANDARD TEST METHOD FOR POUR POINT

Scope

This test method is intended for use on any petroleum product and Bio diesel.

Summary of Test Method

After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of

The specimen is observed is recorded as the pour point.

Significance and Use

The pour point of a fuel specimen is an index of the lowest temperature of its utility for certain applications.

Apparatus

- 1) Test Jar, cylindrical, of clear glass, flat bottom, 33.2 to 34.8-mm outside diameter, and 115 to 125 mm in height.
- 2) The inside diameter of the jar can range from 30.0 to 32.4 mm, within the constraint that the wall thickness be no greater than 1.6 mm. The jar shall have a line to indicate a sample height 54 ± 3 mm above the inside bottom. See Fig. 2.
- 3) Cork, to fit the test jar, bored centrally for the test thermometer.
- 4) Jacket, watertight, cylindrical, metal, flat-bottomed, 115 ± 3 -mm depth, with inside diameter of 44.2 to 45.8 mm. It shall be supported in a vertical position in the cooling bath so that not more than 25 mm projects out of the cooling medium, and shall be capable of being cleaned.
- 5) Disk, cork or felt, 6 mm thick to fit loosely inside the jacket

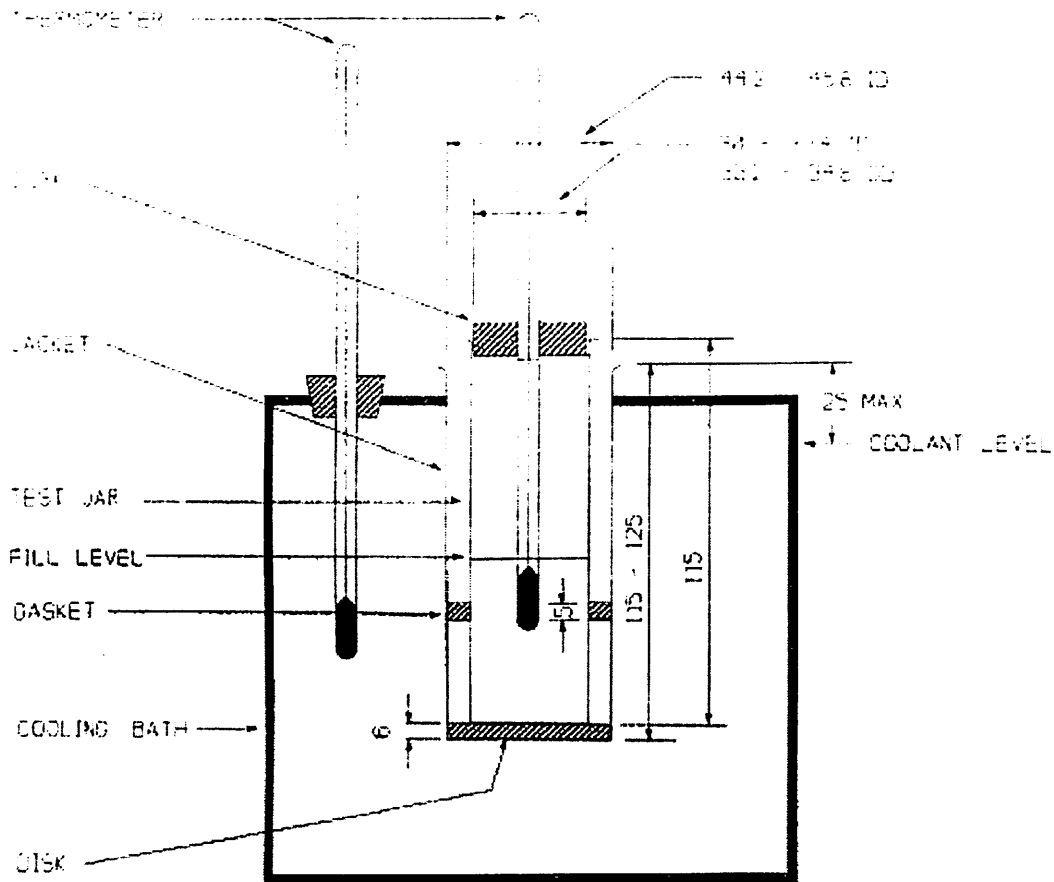


FIG 2 Apparatus for pour point test

- 6) Gasket, to fit snugly around the outside of the test jar and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test jar and hard enough to hold its shape. Its purpose is to prevent the test jar from touching the jacket.
- 7) Bath or Baths, maintained at prescribed temperatures with a firm support to hold the jacket vertical. The required bath temperatures may be obtained by refrigeration if available, otherwise by suitable freezing mixtures. Freezing mixtures commonly used for temperatures down to those shown are as follows:
 - 1) Ice and water - 10°C
 - 2) Crushed ice and sodium chloride crystals - 12°C

- 3) Crushed ice and calcium chloride crystals - 27°C
- 4) Acetone, methyl or ethyl alcohol, or petroleum naphtha chilled in a covered metal beaker with an ice-salt mixture to - 12°C, then with enough solid carbon dioxide to give the desired temperature.

Reagents and Materials

Acetone—Technical grade acetone is suitable for the cooling bath, provided it does not leave a residue on drying. (**Warning**— Extremely flammable)

Calcium Chloride—Commercial or technical grade calcium chloride is suitable.

Carbon Dioxide (Solid) or Dry Ice—A commercial grade of dry ice is suitable for use in the cooling bath.

Ethanol or Ethyl Alcohol—A commercial or technical grade of dry ethanol is suitable for the cooling bath. (**Warning**— Flammable. Denatured, cannot be made nontoxic.)

Methanol or Methyl Alcohol—a commercial or technical grade of dry methanol is suitable for the cooling bath. (**Warning**—Flammable. Vapor harmful)

Petroleum Naphtha—a commercial or technical grade of petroleum naphtha is suitable for the cooling bath. (**Warning** — Combustible. Vapor harmful)

Sodium Chloride Crystals—Commercial or technical grade sodium chloride is suitable.

Sodium Sulfate—a reagent grade of anhydrous sodium sulfate should be used when required.

Procedure

1) Pour the specimen into the test jar to the level mark. When necessary, heat the specimen in a water bath until it is just sufficiently fluid to pour into the test jar.

2) Close the test jar with the cork carrying the high-pour thermometer. In the case of pour points above 36°C , use a higher range thermometer. Adjust the position of the cork and thermometer so the cork fits tightly, the thermometer and the jar are coaxial, and the thermometer bulb is immersed so the beginning of the capillary is 3 mm below the surface of the specimen.

3) For the measurement of pour point, subject the specimen in the test jar to the following preliminary treatment:

a) Specimens Having Pour Points Above -33°C —Heat the specimen without stirring to 9°C above the expected pour point, but to at least 45°C , in a bath maintained at 12°C above the expected pour point, but at least 48°C . Transfer the test jar to a water bath maintained at 24°C and commences observations for pour point.

b) Specimens Having Pour Points of -33°C and Below—Heat the specimen without stirring to 45°C in a bath maintained at 48°C and cool to 15°C in a water bath maintained at 6°C . Remove the high cloud and pour thermometer, and place the low cloud and pour thermometer in position.

4) See that the disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium.

5) After the specimen has cooled to allow the formation of paraffin wax crystals, take great care not to disturb the mass of specimen nor permit the thermometer to shift in the specimen; any disturbance of the spongy network of wax crystals will lead to low and erroneous results.

6) Pour points are expressed in integers that are positive or negative multiples of 3°C. Begin to examine the appearance of the specimen when the temperature of the specimen is 9°C above the expected pour point (estimated as a multiple of 3°C). At each test thermometer reading that is a multiple of 3°C below the starting temperature remove the test jar from the jacket. To remove condensed moisture that limits visibility wipe the surface with a clean cloth moistened in alcohol (ethanol or methanol). Tilt the jar just enough to ascertain whether there is a movement of the specimen in the test jar. The complete operation of removal, wiping, and replacement shall require not more than 3 seconds.

7) If the specimen has not ceased to flow when its temperature has reached 27°C, transfer the test jar to the next lower temperature bath in accordance with the following schedule:

Specimen is at +27°C, move to 0°C bath

Specimen is at +9°C, move to - 18°C bath

Specimen is at - 6°C, move to - 33°C bath

Specimen is at - 24°C, move to - 51°C bath

Specimen is at - 42°C, move to - 69°C bath

As soon as the specimen in the jar does not flow when tilted, hold the jar in a horizontal position for 5 seconds as noted by an accurate timing device and observe carefully. If the specimen shows any movement replace the test jar immediately in the jacket and repeated the test for flow at the next temperature, 3⁰C lower. Continue in this manner until a point is reached at which the specimen shows no movement when the test jar is held in a horizontal position for 5 seconds. Record the observed reading of the test thermometer.

Expression of result

Add 3°C to the temperature recorded in the experiment and report this as the pour point or lower pour point as applicable.

Repeatability

The difference between two test results obtained by the same operator, using the same apparatus, under constant operating conditions, on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 3°C only in one case in 20.

Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 6°C only in one case in 20.

Test Report

The test Report shall contain at least the following information

- d) All details necessary to identify the product tested.
 - e) The result of the test.
 - f) The date of the test.
 - g) Whether the test was determined by an automatic instrument.
- (Jhon Phipps⁹).

CHAPTER 4

In general rheological properties deals with viscosity, shear stress, cloud point and pour point etc. In this work we concentrated only on cloud point and pour point.

STRATEGIES

Based on the literature review we developed the possible strategies. The strategies are given below:

Strategy 1

Controlling of saturates present in the biodiesel.

Routes

1. Use Isopropanol or 2-butanol instead of methanol
2. Ozonation of vegetable oils

Strategy 2

Developing of additives to control the agglomeration of crystals

Routes

1. Usage of metallic additives (MnO_2 and NiO based)
2. Developing the polymers which control the agglomeration of crystals

Strategy 3

Depression in freezing Point

Routes

1. Blending with kerosene, diesel (Petroleum products). Blending with kerosene leads to decrease in cloud point and pour point but significant reduction in calorific value also.

Selection of strategies

The use of secondary alcohols such as Isopropanol or 2-Butanol, leads to incomplete reaction and lower yields of methyl ester. When compared to methanol, the cost of secondary alcohols is high which increases the production cost.

Blending with inferior quality fossil fuel leads to decrease in the calorific value. Now we are having two options. They are,

- i). Blending with diesel.

ii). Addition of additives.

In this project work we analyzed above two options.

ADDITIVES

Additives generally referred to as cold flow improvers or pour point depressants.

CRITERIA FOR THE SELECTION OF ADDITIVES:

- The additive should not produce negative side effects, e.g., they should not promote the formation of water-in-diesel emulsion
- Safety and environmental aspects have to be regarded, as well as the handling properties
- The additive have to be compatible with other diesel additives ready in the market
- Finally, but not less important, the treatment costs per ton diesel fuel should be low.

POUR DEPRESSANTS MECHANISM

Pour point phenomenon can be of two types;

- i) Due to wax congealing
- ii) Due to high viscosity which increases approximately logarithmically with inverse Absolute temperature. (M.C. Dwivedi et al¹⁰)

Mechanism

The first study of the action of pour point depressants was reported Zimmer, Davis & Frolich following the invention of "Para flow". They stated that the gelation of oil is associated with the separation of wax and suggested that a three dimensional wax network was responsible for the gel formation. The "Para flow" they considered prevented the gel formation both by reducing the wax crystal size and by preventing the adsorption of oil by the wax (Himmant Singh¹¹).

Bondi¹² says that "depressants" act by being adsorbed on the newly formed crystal surfaces and thus do not allow the formation of the cohesive structure by preventing the wax crystals from sticking to each other. Leiber suggested that a "selective salvation" is involved, the depressant being a solvating agent for wax which causes it to coagulate and precipitate. Zhuze believes that when adsorption of additives takes place, wax crystal growth is inhibited and additive by steric hindrance prevents crystal aggregation.

Ruehrwein¹³ believes that methacrylate cocrystallizes with wax leaving the polymer back-bone containing the polar group towards the oil side of the interface which prevents further wax from crystallizing on the same nuclei and oil from adsorbing on it.

Gavlin says that the adsorption of the pour point depressants would cause a decrease in the growth rate of that crystal face and thus the accommodation of crystals for inter crystalline growth i.e. reduced by adsorbed additives. Koch believes that adsorption of depressants prevents normal growth.

Chuang - wei chiu in diesel a few polymer adsorption having long hydrocarbon chains have observed to delay observable crystal formation as a petroleum diesel is cooled there additives tend to reduce the visibility of the crystals and not their formation.

CHAPTER 5

EXPERIMENTAL RESULTS & DISCUSSION

The cloud point and pour point analysis were conducted according to ASTM standards. The properties of Biodiesel (A) sample is as follows.

Name	: Mahua methyl ester
Acid value (mg of KOH/g)	= 0.5
Moisture content (%)	= 0.03
Appearance	= clear
Colour	= dark yellow
Flash point °C	= 127
Fire point °C	= 136
Cetane number	=51
Kinematic viscosity @ 40 °C (Cst)	= 5.2
Specific gravity	= 0.865

Initially the cloud point and pour point of bio-diesel fuel was found by the experiment. It was found that sample Bio-diesel has the cloud point of 23 °C and pour point of 15°C.

Diesel Properties

Source: Mathura Refinery

Color : Brownish Yellow

Initially the cloud point and pour point of diesel fuel was found by the experiment. It was found that sample diesel has the cloud point of 6⁰C and pour point of -3°C without additive.

Table 2

S. No	Additive Number	Composition	Ratio
1	28	C ₂₂ :C ₆ :MAN	1:1:0.1
2	32	C ₂₂ :MMA:MAN	25:2:1
3	27.5	C ₂₂ Acrylate:MAN	1:14
4	23	C ₂₂ Acrylate:MAN	1:1
5	21	C ₂₂ Acrylate: C ₆ Acrylate	1:25
6	18	C ₂₂ Acrylate: C ₆ Acrylate	1:6
7	40.5	Acrylic acid: C ₆ Acrylate	1:6
8	41.5	Acrylic acid: C ₂₂ Acrylate:MMA	2:1:8
9	31.5	C ₂₂ Acrylate: C ₆ Acrylate:MAN	20:100:1
10	41	Acrylic acid: C ₂₂ Acrylate	1:6

Note

MMA: Methyl Methacrylate

MAN: Methacrylonitril.

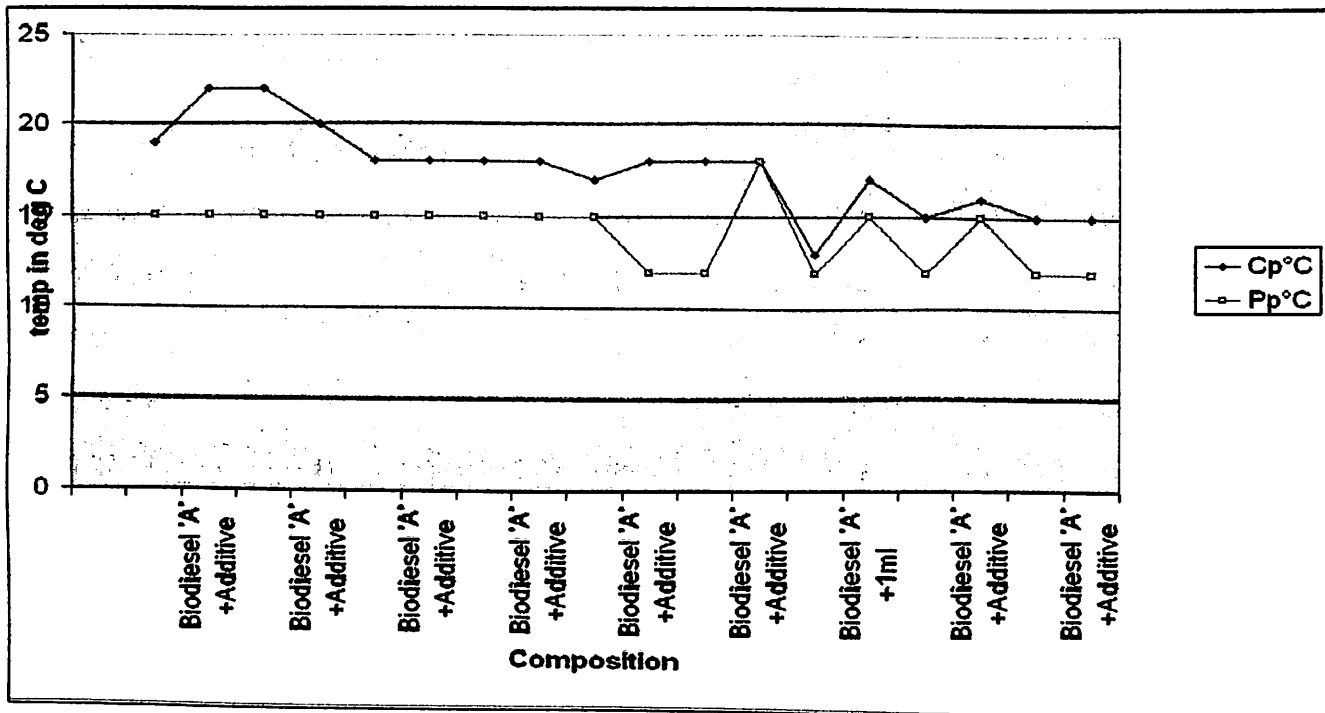
This table shows the composition and ratio of the various additives used in this work. During the experiment the performance of the individual additive as well as mixture of additives were examined. The following table shows the additive response on cloud point and pour point of the bio diesel. Prior to study the performance of the additives, the sample bio diesel cloud point and pour point were studied.

Table 3

Date(dd/mm/yy)	Composition	Additive Concentration			
		500PPM		1000PPM	
		Cp°C	Pp°C	Cp°C	Pp°C
23/03/07	Biodiesel 'A' +Additive 28	22	12	21	15
26/03/07	Biodiesel 'A' +Additive 32	20	15	24	15
28/03/07	Biodiesel 'A' +Additive 27.5	20	18	20	18
29/03/07	Biodiesel 'A' +Additive 23	20	15		
2/4/2007	Biodiesel 'A' +Additive 21	21	18		
3/4/2007	Biodiesel 'A' +Additive 18	19	15	18	15
4/4/2007	Biodiesel 'A' +Additive 40.5	19	18		
9/4/2007	Biodiesel 'A' +Additive 41.5	18	15		

Date(dd/mm/yy)	Composition & Concentration	Cp°C	Pp°C
30/03/2007	Biodiesel 'A' +Additive 23+Additive 31.5(500 ppm each)	19	15
2/4/2007	Biodiesel 'A' +Additive 21+Additive 18 (500 ppm each)	22	15
5/4/2007	Biodiesel 'A' +Additive 18+Additive 28 (500 ppm each)	22	15
5/4/2007	Biodiesel 'A' +Additive 28+Additive 18+ Additive 41 (500 ppm each)	20	15
11/4/2007	Biodiesel 'A' +Additive 28+Additive 18 (250 ppm each)	18	15
11/4/2007	Biodiesel 'A' +Additive 28(375 ppm)+Additive 18 (250 ppm)	18	15
12/4/2007	Biodiesel 'A' +Additive 28(425 ppm)+Additive 18 (250 ppm)	18	15
12/4/2007	Biodiesel 'A' +Additive 28(525 ppm)+Additive 18 (250 ppm)	18	15
12/4/2007	Biodiesel 'A' +Additive 28(650 ppm)+Additive 18 (250 ppm)	17	15
13/04/2007	Biodiesel 'A' +Additive 28(775 ppm)+Additive 18 (250 ppm)	18	12
13/4/2007	Biodiesel 'A' +Additive 28(900 ppm)+Additive 18 (250 ppm)	18	12
19/04/2007	Biodiesel 'A' +Additive 28(900 ppm)+Additive 18 (250 ppm)+500ppm dispersant	18	18
19/04/2007	Biodiesel 'A' +Additive 28(900 ppm)+Additive 18 (250 ppm)+1000ppm dispersant	13	12
20/04/2007	Biodiesel 'A' +1ml dispersant	17	15
20/04/2007	Biodiesel 'A' +Additive 28(100 ppm)+1ml dispersant	15	12
23/04/2007	Biodiesel 'A' +Additive 28(250 ppm)+1ml dispersant	16	15
23/04/2007	Biodiesel 'A' +Additive 28(500 ppm)+1.5 ml dispersant	15	12
23/04/2007	Biodiesel 'A' +Additive 28(500 ppm)+2.5 ml dispersant	15	12

Graph 1



Graph 2

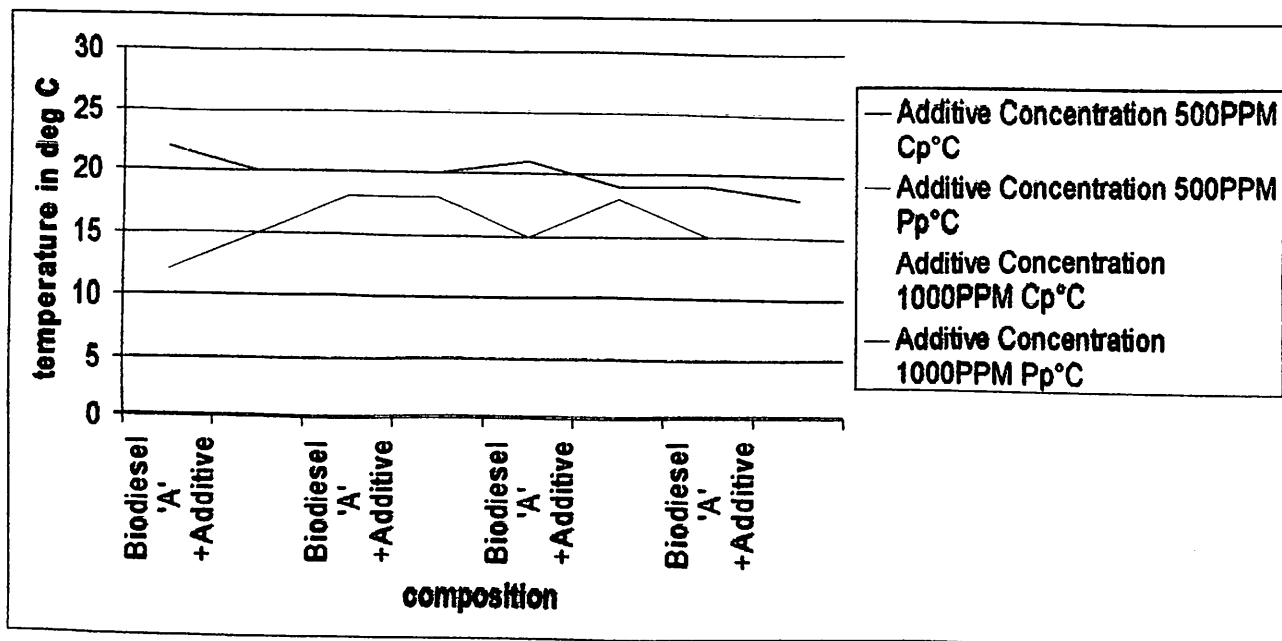
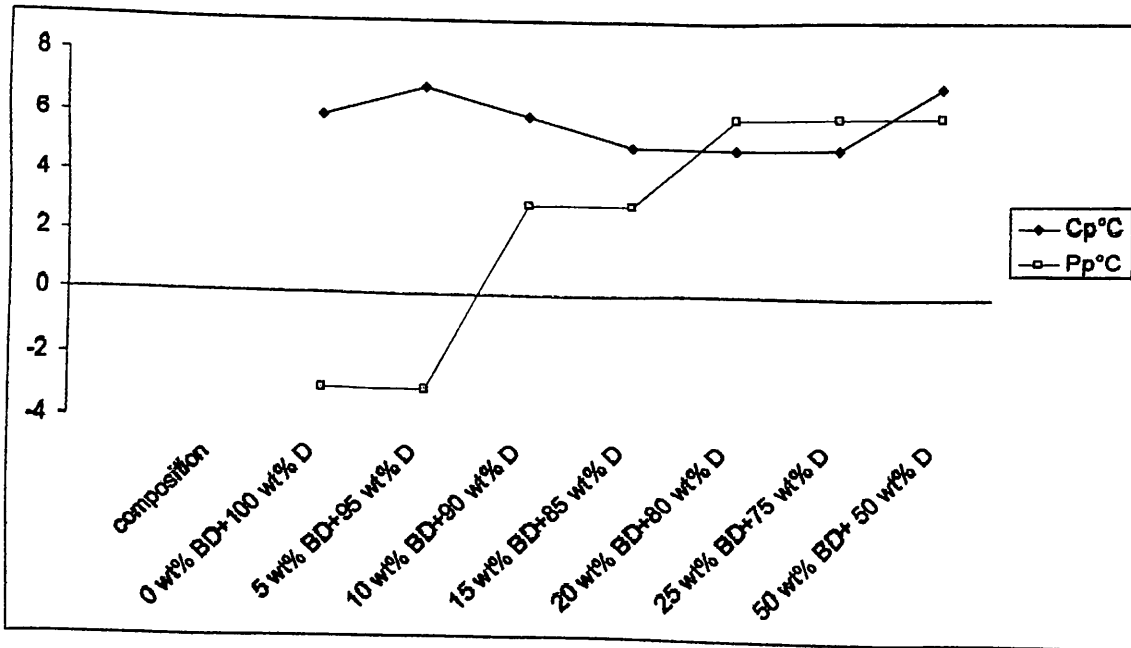


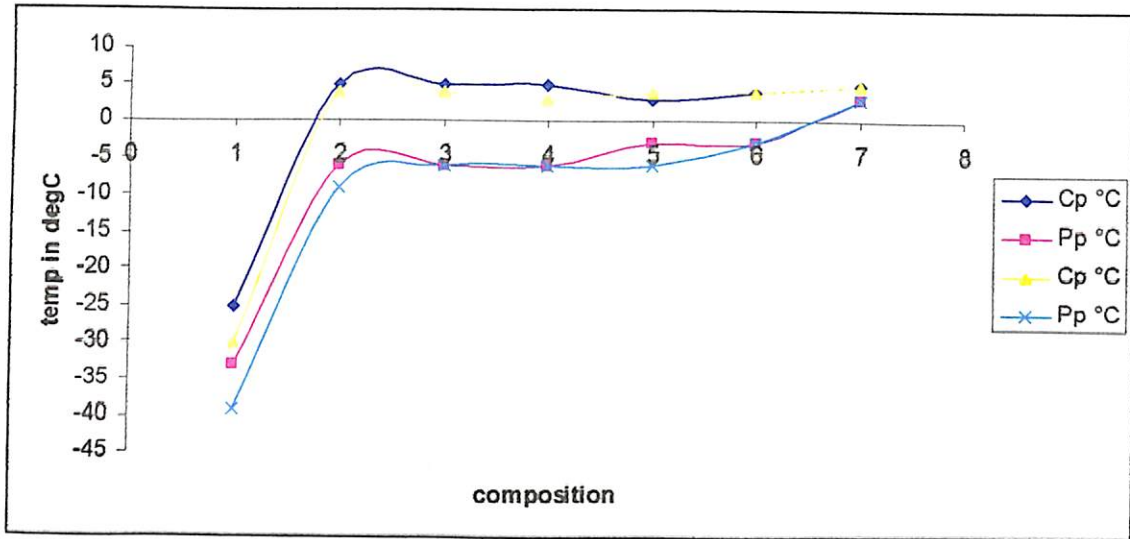
Table 4

Date	composition	Cp °C	Pp °C	concentration of additive 31.5 in ppm			
				500		1000	
				Cp °C	Pp °C	Cp °C	Pp °C
9/4/2007	0 wt% BD+100 wt% D	6	-3	-25	-33	-30	-39
10/4/2007	5 wt% BD+95 wt% D	7	-3	5	-6	4	-9
11/4/2007	10 wt% BD+90 wt% D	6	3	5	-6	4	-6
12/4/2007	15 wt% BD+85 wt% D	5	3	5	-6	3	-6
13/04/07	20 wt% BD+80 wt% D	5	6	3	-3	4	-6
19/04/07	25 wt% BD+75 wt% D	5	6	4	-3	4	-3
20/04/07	50 wt% BD+ 50 wt% D	7	6	5	3	5	3

Graph 3



Graph 4



It has been observed that cloud point and pour point of bio diesel and diesel mix increases with increase in concentration of bio diesel.

We noticed change in crystal morphology with additive 18 + additive 28 combination. The additive 28 concentration of 525 ppm and above with 250 ppm of additive 18, did not show any “gelly crystal” formation at the bottom of the test jar. The crystals formed were adhered on the walls and grows inwardly.

In the case of additive 28 + additive 18 with liquid disperssant we noticed the crystals like “sludge”. In all other cases we observed that, the Gelly crystals formed at the bottom of the test jar.

CHALLENGES

(i) Pour reversion

Some oils show an increase in pour point during long storage i.e., after long aging they solidify at higher temperature than their normal pour point. This phenomenon is known as “pour reversion”.

(ii) Oxidation stability of Bio-diesel

The research on Bio-diesel stability has been put on top priority by voting at annual Bio-diesel technical work shop held at Chicago on 12th Jan and 13th Jan 2005. As Bio-diesel chemically is an ester molecule, there is every possibility that in the presence of air or O₂ it will be hydrolyzed to alcohol and acid. Presence of alcohol will lead to reduction in flash point and presence of acid will increase total acid no. All these make methyl ester relatively unstable on store and cause damage to engine parts. This is why oxidation stability is an important criterion for Bio-diesel.

The stability of Bio-diesel is inferior compared to petro-diesel and therefore doping of Bio-diesel in petro-diesel will affect the stability of fuel significantly. The poor stability of Bio-diesel is also because of the double bonds in the fatty acids, which may lead to gum formation. In either of the cases the product will become off spec. therefore, it was considered to include a limit for oxidation stability in the existing quality standard for Bio-diesel.

At most in all Bio-diesel fuel significant amount of esters of oleic, linolenic, and linoleic acid are present and the trend of increasing stability was linolenic < linoleic < oleic.

These esters undergo auto-oxidation with different rates depending upon the number and position of the double bond and results in formation of a series of by products like, acids, esters, aldehydes, ketones, lactones etc.

During the oxidation process, the fatty acid methyl ester usually forms a radical next to the double bond. This radical quickly binds with the oxygen in the air, which is a bi radical. This forms peroxide radical. The rapid radical destruction cycle begins after that. This peroxide radical immediately creates a new radical from the fatty acid methyl ester, which in turn binds with oxygen in the air.

Then the destructive radical auto-oxidation cycle starts. During this process, up to 100 new radical are created quickly from one single radical, meaning that decomposition occurs at an exponentially rapid rate and results in the formation of a series of by products. These species formed during the oxidation process cause the fuel to eventually deteriorate. Finally the oil spoils and became rancid very quickly.

Sample bio-diesel (A) has the cloud point and pour points of 23°C and 15°C respectively. Mixture of additive (900 ppm of additive 28+250 ppm of additive 28 and few ml of liquid dispersant) significantly reduced the pour point up to 12°C . Some additives show very little effects on pour depression. The additives like 27.5, 23, 21, 18, 40.5 shows negative effects on pour depression. The additive combinations such as 21+18, 18+28+41, 23+31.5 has no effect on pour point. The additive mixture 18+28 showed little positive response on pour depression. (Refer table 3)

Graph 1 indicates the additive response on pour point and cloud point of various additives up to the concentration of 1000 ppm.

Graph 2 indicates the additive response on cloud point and pour point of various mixtures of additives.

Bio-diesel Blend

5% bio-diesel blend has the lowest pour point of -3°C . 5% bio-diesel blend with additive 31.5 has the lowest pour point of -9°C . The additive 31.5 significantly reduced the pour point of bio-diesel. The blends pour point increases with increasing bio-diesel content. At 50% bio-diesel blend has the pour point of 6°C without additives and 3°C with additive 31.5 (upto 1000 ppm). It has been observed that the effect of additive on pour point depression is significantly reduced with increasing concentration of bio-diesel.

The table 4 shows that the changes in the cloud point and pour point with bio-diesel concentration in diesel with out any additives.

Graph 3 indicates that the changes in cloud point and pour point with bio-diesel concentration.

Graph 4 indicates the additive 31.5 response on bio-diesel in diesel mix.

CONCLUSION

It has been found that the optimum mixture is 900 ppm of additive 28+250 ppm of additive 18 and few ml of liquid dispersant. The pour point of bio-diesel – diesel mix increases with concentration of bio-diesel. The additive 31.5 response on bio-diesel – diesel mix is reduced with increased bio-diesel concentration. The optimum mix is 5% bio-diesel – diesel mix which has the lowest pour point of -9°C with additive 31.5.

FUTURE DIRECTION

Development of Multi Functional Additives (MFA) package contains any or all the components as given below.

- i) Flow Improvers (CP, CFPP, PP Depressant)
- ii) Detergents
- iii) Antifoam
- iv) Lubricity Improvers
- v) Oxygen Stabilizers
- vi) Corrosion Inhibitor, odorant and smoke suppressant etc.

The development of Multi Functional Additives (MFA) for Bio Diesel is necessary and urgent. More attention is required to develop MFA for Bio Diesel.

BIBLIOGRAPHY

- [1]. Ali Keskin, Metin Guru, Duran Altı Parmak, Bio-diesel Production from Tall Oil with Synthesized Mn and Ni Based Additives: Effects of Additives on fuel consumption and emissions, *Fuel* 86(2007) pg no 1139-1143.
- [2]. Hiroaki Imahara, Eiji Minami, Shiro Saka, Thermodynamic study on cloud point of Biodiesel with its fatty acid composition, *Fuel* 85(sep 2006) pg no 1666-1670
- [3]. Chuang-Wei Chiu, Leon G.Schumacher, Galen J.Suupes, Impact of cold flow improvers on soya bean Biodiesel blend, *Biomass and bio energy* 27 (2004) pg no 485-491.
- [4]. Nestor U. Soriano Jr, Veronica P. Migo, Masatoshi- Matsumura, Ozonized vegetable oil as pour point depressant for neat Biodiesel, *Fuel* 85(2006) pg no 25-31.
- [5]. Rakesh sarin Meeta Sharma, S.Sinharay, R K. Malhotra Jatropha- Palm Biodiesel Blends: An optimum mix for Asia- IOCL R&D research center Faridabad - *Fuel* (2007) in press.
- [6]. Bredakegel, Ales, Hribernik, Experimental analysis of injection characteristics using Biodiesel fuel, *Energy and Fuels* volume 20, no 5 sep/oct 2006.
- [7]. P.P.Bhojvaid, Biofuels towards a greener and secured energy future, TERI press 2006.
- [8]. Jhon Phipps, Standard methods for analysis and testing of petroleum and related products and British standard 2000 parts -2006. volume1, energy institute, UK, 219.1 to 219.6.
- [9]. Jhon Phipps, Standard methods for analysis and testing of petroleum and related products and British standard 2000 parts -2006. volume2, energy institute, UK, IP15/95 (2004).
- [10]. M.C. Dwivedi, R.Vipradas, DR.G.K.Trivedi, Alkylate pour point depressant – effect on chemical structure-, IIT-B, 3rd Lubricant, additives, waxes and petroleum specialty products (LAWPSP) Symposium,1982 volume 3, no 3, pg no A-21.
- [11]. Himmant Singh, Influence of degree refining of lubricating oil base stocks on additive response, Feb 1980, Doctoral thesis, IIP, Dehradun.

- [12]. Bondi. A, Petrol, Refines, 22(9), 267 Sep 1943.
- [13]. Ruehrwein R.A., Proceedings of 3rd world petroleum congress, Hague section 7, pg no 423, 1951.
- [14]. M.E. Gonzalez Gomez, R. Howard-Hildige, J.J. Leahy, B. Rice Winterization of waste cooking oil methyl ester to improve cold temperature fuel properties- -Fuel 81 (2002) 33-39.
- [15]. S.L. Dmytryshyn, A.K.Dalai, S.T. Chaudhari, H.K. Mishra, Synthesis and characterization of vegetable oil derived esters: evaluation for their diesel additive properties- M.J.Reaney-Bioresource Technology 92 (2004) 55-64.
- [16]. John W. Goodrum & Mark A. Eitcman, Physical properties of low molecular weight triglycerides for the development of bio-diesel fuel models, Bioresource Technology, 56 (1996) 55-60.