SOME STUDIES ON SURFACE TENSION, VISCOSITY AND BULK MODULUS OF COMPRESSIBILITY OF BIODIESELS BY DEVELOPING MATLAB MATHEMATICAL MODELS

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UTKARSH SINGH

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Under the supervision of

Dr. Naveen Kumar

PROFESSOR

Department of Mechanical, Production and Industrial engineering

DELHI TECHNOLOGICAL UNIVERSITY

(Formerly Delhi College of Engineering)

Main Bawana Road, Delhi – 110042

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Utkarsh Singh

M.Tech (Thermal engineering)

2K17/THE/19

CERTIFICATE

I hereby certify that the project Dissertation titled **" SOME STUDIES ON SURFACE TENSION, VISCOSITY AND BULK MODULUS OF COMPRESSIBILITY OF BIODIESELS BY DEVELOPING MATLAB MATHEMATICAL MODELS "** which is submitted by **Utkarsh Singh (2K17 / THE /19)** to the department of Mechanical, Production and Industrial Engineering, Delhi Technological University , Delhi in partial fulfillment for the award of Master of Technology in Thermal engineering, is a record of the project work carried by him under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this degree or elsewhere.

Prof. Naveen Kumar

Mechanical Engineering Department

Delhi Technological University

CANDIDATE'S DECLARATION

I UTKARSH SINGH , 2K17 /THE/19 student of M.Tech(Thermal Engineering) hereby declare that the project dissertation titled **" SOME STUDIES ON SURFACE TENSION, VISCOSITY AND BULK MODULUS OF COMPRESSIBILITY OF BIODIESELS BY DEVELOPING MATLAB MATHEMATICAL MODELS"** which is submitted by me to the Department of Mechanical, Production and Industrial Engineering , Delhi Technological University , Delhi in partial fulfillment of the requirement of the degree of Master of Technology is original and not copied from any source without citation. This work has not previously formed the basis for the award of any Degree, Diploma, Associate-ship, Fellowship and other similar title and recognition.

Place: Delhi **Utkarsh Singh**

Date: M.Tech (Thermal Engineering)

2K17/THE/19

ABSTRACT

The future for biodiesels relies heavily on the optimization of the thermo-physical properties such as the surface tension, viscosity and bulk modulus of compressibility of biodiesels. These three properties play a crucial role in the atomization of fuel, pre – combustion of fuel, knocking tendency and ignition timing of the fuel respectively. Estimation of the properties could give a good insight about these properties and also about what can be done further to alter those values to be in the ASTM range defined. Hence a proper understanding of these parameters with their values is essential. The values of surface tension, viscosity and bulk modulus of compressibility can be predicted by developing mathematical models which function on the values of properties of the biodiesel such as density, FAMEs composition of biodiesel in mass fraction, temperature, speed if sound in biodiesel, individual values of surface tension and viscosity of FAMEs of the biodiesel etc. For prediction of surface tension, three models in MATLAB have been developed, a single model in MATLAB for prediction of viscosity of biodiesels and a single model in MATLAB for prediction of bulk modulus of compressibility of biodiesels. The values of the properties were estimated and then made to compare with the values of those properties found experimentally using various equipments mentioned in this thesis. The biodiesels taken into consideration for value prediction of properties on MATLAB models are: karanja, jatropha, soybean, palm, sunflower and rapeseed. The FAMEs composition of biodiesels, individual values of surface tension and viscosity of FAMEs have been taken from literature survey.

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NOMENCLATURE

NOMENCLATURE USED IN MATLAB CODE

BDF	stores the biodiesel name
composition_BDF	stores the mass fraction of FAMEs of the biodiesel
pchallen	stores allen parachors value
pchknotts	stores knotts parachors value
density	stores density of biodiesel
molweight	stores molecular weight of biodiesel
st1	stores surface tension value using Allen parachors
st2	stores surface tension value using Knotts parachors
z_avg	stores average number of carbon atoms of FAMEs of the biodiesel
m_avg	stores average number of double of FAMEs of the biodiesel
temperature	stores temperature value
st3	stores surface tension value according to Gibbs free energy model
fames_st	surface tension value of individual FAMEs
st4	surface tension value according to Dalton model
bdf_viscosity	stores value of viscosity of biodiesel
biodzl	stores biodiesel name for bulk modulus model
densitybdf	stores density of biodiesel
sos_fame	stores value of speed of sound in different FAMEs
sos_bdf	speed of sound in biodiesel
bulk_modulus	stores value of bulk modulus of compressibility of bioidesels

NOMENCLATURE USED IN THESIS

σ	surface tension of liquid compound
P	parachor value of liquid compound
σ_l	density of liquid fuel
σ_v	density of vapours phase of fuel
P_{bdf}	parachor value of biodiesel
X(i)	mass fraction of FAMEs of biodiesel
P_{ch}(i)	parachor value of individual FAMEs
γ	surface tension of biodiesel
ρ	density of biodiesel
M_w	molecular weight of biodiesel
ΔG	Gibbs free energy
ΔG_f	Gibbs free energy of functional group
$\Delta G_1 \ldots \Delta G_z$	Gibbs free energy of methyl group
z	number of carbon atoms of FAMEs
A	surface area of interacting liquids
T	temperature
P	pressure
ΔH	enthalpy
ΔS	entropy
ΔH_f	enthalpy of functional group
m	number of double bonds

Z_{avg}	average number of carbon atoms of the FAMEs of the biodiesel
M_{avg}	average number of double bonds of the FAMEs of the biodiesel
$\gamma(i)$	surface tension value of individual FAMEs
μ_m	viscosity of biodiesel
Gij	interaction parameter between two liquids
$\mu(i)$	viscosity value of individual FAMEs
K_s	bulk modulus of compressibility of biodiesel
U	velocity of sound
U_{bd}	velocity of sound in biodiesel
P_t	total force acting on ring
P_r	weight of the ring
R	radius of the ring
f	correction factor
υ	kinematic viscosity
k	constant for the capillary tube
t	time in seconds
V_i	volume of pycnometer after pressure application
V_{i-1}	volume of pycnometer before pressure application
P_i	pressure acting on the pycnometer after pressure is applied using helium
P_{i-1}	pressure acting on the pycnometer before pressure is applied using helium

CHAPTER 1

INTRODUCTION

Environmental, economic and geopolitical situations including increasing global warming, surging of crude oil prices and depletion of natural petroleum reserves has lead to an increase in the demand of renewable bio-fuels. It is so because of their renewable nature, lower particulate emissions, better lubrication characteristics, higher flash point, good potential for carbon dioxide reduction, bio-degradability , their non toxic nature and the absence of sulfur and aromatic compounds which could cause even more pollutant emission [1]. This renewed interest in using biofuels particularly in vegetable oil based fuels requires some measures to overcome the problems related poor atomization characteristics which further depends upon the fuel properties such as the surface tension, viscosity and bulk modulus of biodiesels. According to ASTM standards, biodiesels are mono-alkyl (methyl or ethyl) esters of long chain fatty acids (FAMEs) which are derived from vegetable oils and animal fats [1]. The biodiesel in general is lesser in complexity than diesel in terms of molecular composition. Biodiesel comprises of only six to seven methyl or ethyl esters.[2] However, it has fuel bound oxygen atoms and hence possesses a higher degree of unsaturation compared to diesel.

The major problems associated with biodiesel fuels are higher viscosity, higher surface tension, higher bulk modulus, poor fluid flow, poor atomization characteristics, higher particulate characteristics, wider variations in feedstock and oxidation stability. Hence the fuel properties of biodiesel need to be improved. The aim of this project is to predict the values of surface tension, viscosity, and bulk modulus of biodiesels using mathematical models made on MATLAB. These mathematical models are based on the composition of the biodiesels , their molecular weight, density, parachor values of individual FAMEs , average number of carbon atoms and average number of double bonds comprising the biodiesel , temperature, surface tension value of individual FAMEs, viscosity value of individual FAMEs and speed of sound in biodiesels.

The importance of this project is that if it becomes possible to predict the values of surface tension, viscosity and bulk modulus of any biodiesel closer to the actual value (found experimentally) by knowing its composition and density, then there may be absolutely no need to opt for expensive and cumbersome testing methods, equipments, programs (codes) for determining the property value of the vegetable oil based fuel used in a compression ignition engine.

1.1 SURFACE TENSION OF BIODIESELS

Surface tension is one of the major physical properties of liquid fuels which affects the atomization of fuel in compression ignition engines. Better atomization, proper mixing helps in complete combustion of fuels which thereby increases engine efficiency and reduces pollutant emission. A balanced value of surface tension is essential for proper atomization in direct injection (DI) engines. Higher surface tension value of the fuel hinders in proper droplet formation leading to inefficient atomization [8]. To predict the surface tension value of biodiesel three mathematical models have been developed in MATLAB software namely 'The Parachor based model' ,' The Gibbs Free Energy model' and the' Dalton Type Mass Average model'.

1.2 VISCOSITY OF BIODIESELS

The atomization process, particularly in the initial stages of combustion in a diesel engine relies in a significant manner on fuel's viscosity. The viscosity value of biodiesel should be low or else it interferes with injector operation which leads to poorer atomization in the combustion chamber causing injector problems such as injector choking, oil ring sticking , thickening and also increased carbon deposits [3]

To predict the value of viscosity, a mathematical model has been coded on MATLAB software - ' The Grunberg- Nissan model'.

1.3 BULK MODULUS OF COMPRESSIBILITY OF BIODIESELS

The bulk modulus of compressibility of fuels have a direct impact on the hydraulic behavior of fuels during the injection of fuel. When the fuel is injected into the engine at high pressures through the injector manifold, the bulk modulus of compressibility tells us about the reduction in volume which is commonly referred to as dilatation. The differences in the value of bulk modulus of compressibility with the composition of fuel is of particular interest. An increase in the value of bulk modulus of compressibility is related to advance in injection timing. This leads to earlier needle lift in the pump nozzle type fuel injection system [15].

To predict the value of bulk modulus of compressibility of biodiesels , a mathematical model has been developed which would work on the values of some physical properties such as surface tension value, density value and the speed of sound in biodiesels. The speed of sound in the biodiesel can be calculated by the combined usage of Aeurbach's model and the average mixing rule.

The above mentioned mathematical models on MATLAB have been developed and the values of surface tension, viscosity and bulk modulus generated by those models have been compared with the experimental data taken from literature.

CHAPTER 2

LITERATURE REVIEW

2.1 SUMMARIZATION OF VARIOUS AUTHORS WORK

In this chapter a comprehensive literature survey has been done which describes methods to predict the value of surface tension, viscosity and bulk modulus of compressibility of biodiesels from the data of fatty acid methyl ester (FAMEs) composition of biodiesels. Biodiesel is a mixture of different FAMEs. Each of the FAMEs has its own individuality in terms of properties such as the individual surface tension value, viscosity value, speed of sound in individual FAMEs, molecular weight etc. Hence each FAME component contributes to the overall value of the above mentioned property. Some of the important FAMEs present in almost every biodiesel are-

Table 1: Various Types of major FAMEs of biodiesel

Acronym	Systematic Name
C8:0	Methyl caprylate
C10:0	Methyl decanoate
C12:0	Methyl laurate
C14:0	Methyl myristoleate
C16:0	Methyl palmitoleate
C18:0	Methyl stearate
C18:1	Methyl oleate
C18:2	Methyl linoleate
C18:3	Methyl linolenate
C22:1	Methyl erucate

Some of the literatures taken into consideration for the purpose of this thesis are discussed below:

Hamed et. al studied different models named ‘The Wilson model’, ‘the non- random two liquid (NRTL) model’ and the ‘Wilson-NRF model’ based on composition of biodiesel and made an estimation of the values of density, viscosity and surface tension of biodiesels . The models were based on thermodynamics and have been used in correlating the thermo-physical properties for 215 experimental points. The average absolute deviation (AADs) of the correlated density of biodiesels for the Wilson model is 0.0141, for the NRTL model is 0.0136 and for the Wilson-NRF is 0.0148. The average absolute deviation (AADs) of the correlated viscosity of biodiesels for the Wilson model is 0.638, for the NRTL model is 0.547 and for the Wilson-NRF is 0.621. The average absolute deviation (AADs) of the correlated surface tension of biodiesels for the Wilson model is 0.402, for the NRTL model is 0.392 and for the Wilson-NRF is 0.479. Out of these models , the NRTL model estimated the physical properties of biodiesels with most accuracy when compared to the data in the literature.[1]

Cecil A.W. Allen et al. studied the surface tension of biodiesels. The paper presented a method to estimate the value of surface tension of biodiesel fuels on the basis of its fatty acid methyl esters (FAMEs) composition. A number of binary, ternary and quarternary mixtures of fatty acid methyl and ethyl esters were prepared and further gas chromatographic standards (GC) were also prepared. It was found out that a mass average equation estimated the surface tension of the mixtures within $\pm 3.4\%$ of the values measured experimentally. Six biodiesels namely coconut, palm, rape, soybean, canola and peanut’s samples were prepared and their fatty acid methyl composition was found out by GC technique. The average mass equation for prediction of surface tension of these biodiesels estimated it with an error of 2-6% higher than the measured value. These results show that the differences in surface tension value between biodiesels was not the main cause of the reported differences in engine tests.[2]

Suriya Phankosol et. al. Surface tension being an important thermophysical property of biodiesels plays a mandatory role in atomization and proper and complete combustion of the fuels in the compression ignition engine. In this study, the Martin’s rule of additivity of free energy is applied to describe the free energy of interfacial interaction of a liquid. Finally, an equation , surface tension $(\gamma) = 60.211 - 0.4307z \quad 0.1125T + 0.00207zT + 3.676m - 0.00893mT$ was derived for prediction of the surface tension of the individual fatty acid methyl ester (FAME), where T, z and m are absolute temperature, number of carbon atoms and number of double bond(s) of fatty acid, respectively. When this equation was used for prediction of the surface tension of the individual FAMEs, the deviation range was 0.03–5.54% and the average absolute deviation (AAD) was 1.32% at temperatures between 20˚C and 100˚ C. Also, the propounded equation has been used for the prediction of the surface tension of a biodiesel. Here first of all, the average carbon numbers and average number of double bonds of the biodiesel was calculated and was used in place of z and m, respectively. The predicted values of surface tension of biodiesels at temperature range between 30˚C and 80˚ C were in accordance with the values taken from the literature. The deviation range was 0.10–5.60% and the AAD was 2.1%.[3]

Thangaraja J et. al. This work focused on vegetable oil and biodiesel as being alternative fuels to diesel fuel as they have more preferable engine characteristics and are of renewable nature. Thangaraja J profounded methods for calculating the value of surface tension of biodiesels and vegetable oil on the basis of the fatty acid methyl ester (FAME) composition of the biodiesels and vegetable oil. In this work , the value of surface tension of fatty acid methyl esters were first calculated using appropriate property equations which is available through literature review. These equations/empirical correlations were validated after being compared suitability of with the measured data found experimentally. An average rule of mixing in which each individual component of biodiesel and vegetable oil (FAME) is weighted was utilized to calculate the value of surface tension of the biodiesel and vegetabe oils . The estimated and measured surface tension values of karanja, palmolein and coconut are compared and it was found out that the readings agreed within a range of 7% over a temperature range of 80˚C. The ramifications of transesterification of triglyceride and variations of compositional data on the thermophysical properties like surface tension, viscosity of biodiesel are also analysed in this work.[4]

Thomas A Knotts et. al. Correct integration of enterprized quantitative structure-property relationship (QSPR) software with an assessed database happens to create a robust tool for development of thermophysical properties such as viscosity, density, surface tension etc. and correlations between them. By putting data quality codes in the DIPPR (Design Institute for physical properties) relation database, a training set of property values within a range of predefined accuracy level could be found out to be used in the QSPR regression software Now this could provide a good basis for fast development of the QSPR correlations of known certainty and chemical domain.

Efforts were made to correlate the property of parachor in terms of atomic and structural properties for which a training set was used although it was limited in temperature and scope. Moreover, different types of molecular descriptors were used which were complied with the accuracy of the training set found from the DIPPR database, and their additive increments to the parachor were analysed from 8697 values of surface tension with uncertainty less than 5% for 649 different compounds. Now this produced a best fit correlation with an average absolute deviation (AAD) of 3.2%.[5]

A.B. Chhetri et. al. This work presented the experimental findings of surface tension measurement of diesel fuel and also jatropha, soapnut, and canola biodiesel fuels. To measure the equilibrium surface tension value of diesel and biodiesel fuels at high temperatures and pressure , the equipments used were high pressure pendant drop equipment (PD-E 1700) and drop shape analysis (DSA 100 V1.9) were used .Further, these surface tension tests were conducted in a nitrogen gas environment. The surface tension of diesel and biodiesel fuels showed clear linear variations with pressures and temperatures. Also, a regression model was made using the data from the measurement for each of the fuels.[6]

Lucy D.A. Chumpitaz et. al. In this work surface tension for four fatty acids (lauric, myristic, palmitic, and oleic) and two triglycerides (tricaprylin and tripalmitin) was measured as a function of temperature. The authors performed the measurement of surface tension using a K12 version. 3.1 (Kruss GmbH) tensiometer within a temperature range from 20˚C (or the melting point of each substance) upto 90°C. Further, the Van- Der Waals-type correlation’s constant and linear equations were presented. The equations were found to be moderately accurate, with mean deviations within 0.570%. These correlation constants were found to be valuable in the designing and evaluation of the process equipment, especially that which involved liquid-gas contact like stripping and distillation columns, reactors, deoderizers and equipment for physical refining.[7]

Samuel V.D. Freitas et. alThe aim of this work was to present new density data for different biodiesels and use the reported data to evaluate the predictive capability of models previously proposed to predict biodiesel or fatty acid methyl ester densities. Densities were measured here for 10 biodiesel samples, for which detailed composition is reported, at atmospheric pressure and temperatures from 278.15 to 373.15 K. Density dependence with temperature correlations was proposed for the biodiesels, and isobaric expansivities are presented. The new experimental data presented here were used along with other literature data to evaluate predictive density models, such as those based on Kay's mixing rules and the GCVOL group contribution method. A comparison between biodiesel densities produced from similar vegetable oils, by different authors, highlights the importance of knowing the detailed composition of the samples.. It is shown that it can predict the densities of biodiesel fuels with average deviations less than 0.4%.[8]

Gerhard Nothe et. al. The properties of the various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel. In turn, the properties of the various fatty esters are determined by the structural features of the fatty acid and the alcohol moieties that comprise a fatty ester. Structural features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation, and branching of the chain. Important fuel properties of biodiesel that are influenced by the fatty acid profile and, in turn, by the structural features of the various fatty esters are cetane number and ultimately exhaust emissions, heat of combustion, cold flow, oxidative stability, viscosity, and lubricity.[9]

Maria Jesus Ramos et. al. The aim of this work was to study the influence of the raw material composition on biodiesel quality, using a transesterification reaction.Ten refined vegetable oils were transesterificated using potassium methoxide as catalyst and standard reaction conditions (reaction time, 1 h; weight of catalyst, 1 wt.% of initial oil weight; molar ratio methanol/oil, 6/1; reaction temperature, 60 C). Biodiesel quality was tested according to the standards. Some critical parameters like oxidation stability, cetane number, iodine value and cold filter plugging point were correlated with the methyl ester composition of each biodiesel, according to two parameters: degree of unsaturation and long chain saturated factor. Finally, a triangular graph based on the composition in monounsaturated, polyunsaturated and saturated methyl esters was built in order to predict the critical parameters of European standard for whatever biodiesel, known its composition.[10]

Kanit Krisnangkura et. al. The carbon number or equivalent carbon number (ECN) of fatty acid methyl esters (FAMEs) separated on a 30-m x 0.32-mm-i.d. Omegawax 320 capillary column is calculated directly from the retention data. When the described equation was used to identify FAMEs in a mixture of FAMEs from rambutan and para-rubber seed oils, the calculated ECN values are very close to the widely accepted equivalent chain length values described in the literature. Hence, the equation can probably be used as an identification tool for FAMEs.[11]

N Sirimongkolgal et. al. Density is important physical property of a liquid. In this work, correlation of density of fatty acids (FA) is correlated to the Martin's rule of free energy additivity for estimated density from either (1) its number of carbon atoms (of fatty acid, z) and number of double bonds (nd) or (2) its saponification number (SN) and iodine value (IV). Data collected from literatures were used to validate, and support the proposed models. The proposed equations are easy to use and the estimated density values of FA at different temperatures form agree well with the literature values. The average absolute deviation of density of FA at 297.05 and 394.25 K is 0.17%.[12]

Mariana B. Oliviera et. al. Despite the importance of surface tension, there are very few data on the surface tension of biodiesels or fatty acid esters from which biodiesels are composed and even less are available on its temperature dependence. To overcome this limitation, this work reports experimental surface tensions for 10 biodiesel fuels in a wide temperature range and evaluates the ability of two models to predict these data: the parachor-based MacLeodSugden equation and the density gradient theory based on the cubic-plus-association equation of state (CPA EoS). It is shown that both models provide an acceptable description of the experimental surface tension of the biodiesel fuels studied, with an overall average relative deviation (OARD) of 7.7% for the MacLeodSugden equation using the Allen's parachors and 1.3% with the Knotts' parachors, while the CPA EoS combined with the gradient theory presents an OARD of 9.7%. Given the scarcity of data on surface tensions, these models prove to be useful for predicting surface tensions and their temperature dependence for biodiesel fuels.[13]

Qing Shu et. al. To predict the viscosity of any given biodiesel fuel (FAME mixture), a novel topological index based on the distance matrix and adjacent matrix of the molecular structure is proposed. The new topological index can reflect the information of the molecular structure for fatty acid methyl ester (FAME), such as the size of molecular, unsaturated bond and branch degree. Combined with the modified Grunberg–Nissan or Hind equation, the topological index values of the FAME mixture were calculated. Then, relates the topological index values of the FAME mixtures with the viscosities of them, two linear regression equations were obtained. Using these regression equations, the viscosity of biodiesel fuels were predicted. The results show the modified Grunberg–Nissan equation with a higher precision of prediction than the Hind equation regression equation.[14]

David Morris et. al. In this paper, the interaction between the bulk modulus of compressibility of various fuel samples and its effect on fuel injection timing has been examined. The fuels considered range from soy oil derived biodiesel, unrefined soybean oil, and paraffinic solvents to ultralow-sulfur and conventional diesel fuels. Both the impact on injection timing and the variation in the bulk modulus of compressibility are measured. The presented work confirms that the higher bulk modulus of compressibility of vegetable oils and their methyl esters leads to advanced injection timing with in-line pump-line-nozzle fuel injection systems. This has been shown in the literature to contribute to the well-documented increase in NO*x* emissions with the use of biodiesel fuel. An opposite trend, a retarding of injection timing, is observed with paraffinic fuels, because they have a lower bulk modulus of compressibility than conventional diesel fuels. This supports the observation that paraffinic fuels such as Fischer-Tropsch diesel yield lower NO*x* emissions.[15]

Magin Lapuerta et. al In this work, the bulk modulus of biodiesels was measured by means of a specific apparatus that compresses a fuel sample in a high-pressure closed bottom capillary tube (a pycnometer) and by observing the height change in the column of fluid as pressure is increased over a range of pressures from 3 to 33 MPa. The bulk modulus of a conventional diesel fuel, a soybean oil derived biodiesel, and a hydrotreated soybean oil diesel fuel, together with that of their ternary blends, were measured. Water served as the calibration fluid, and measurements were made at 38 °C. All the fuels tested displayed substantially lower isothermal bulk modulus than water. There are observed differences between these fuel samples, with biodiesel displaying much lower compressibility than both the conventional diesel fuel and the hydrotreated oil An optimized correlation has been obtained to predict bulk modulus from the volume proportions of the three fuels tested. [16]

Jaime B. Santos et. al The property that has an important effect on the fuel injection timing is the speed of sound which is related to the isentropic bulk modulus of the fuels. In this work the speed of sound of six fatty acid methyl esters (FAME = laurate (MeC12:0), myristate (MeC14:0), palmitate (MeC16:0), stearate(MeC18:0), oleate(MeC18:1), linoleate(MeC18:2)) and six biodiesel fuel samples were measured using a non-intrusive ultrasonic methodology. The measurements for FAMEs were made at atmospheric pressure from a minimum of 288.15 K to a maximum of 353.15 K, and in the temperature range 298.15–353.15 K for biodiesel samples. The uncertainty of the measurements was estimated as less than ±1%. These data along with the density of biodiesels were used for calculating the value of bulk modulus of compressibility of biodiesels. The results for molecular compressibility evidenced that this property is almost independent of the temperature in the temperature range of calculations both for FAMES and biodiesel. Linear relationships were established between the molar compressibility and the molecular weight for FAMES and biodiesel.[17]

R. G. Ackman et. al. The current work presented a method, which has been experimentally verified, for estimating the viscosity value of biodiesel fuels from the information of their fatty acid composition. The applicability of a logarithmic mixture equation was checked and verified using known mixtures of standard fatty acid esters and natural biodiesels. The viscosities were estimated from their composition values and were found to be within 3.7% of their experimentally measured values. The fatty acid compositions of six typical oils were analysed by mixing fatty acid methyl ester (FAME) standards in appropriate amounts. The viscosity values of these mixtures were also estimated to be within 2.1% of their experimentally measured values. The viscosities of fifteen biodiesel types were then predicted based on their fatty acid composition as published in the literature and were found to vary as much as 100%. The viscosity of biodiesel fuels reduce considerably with increase in unsaturation. The viscosity of biodiesel fuels was significantly affected by even small amounts of glycerides.[18]

Vivek and A. K. Gupta This study was initiated to investigate the feasibility of karanja oil as a source of biodiesel. Main objectives of this study was to investigate of karanja oil as a source of biodiesel. Further, optimization of other parameters were were done for high yield of biodiesel from karanja oil. The optimum conditions which were found were: Temperature around 70˚C , Pressure 1 atmospheric pressure, ratio of reactants

10:8 (moles of oil: moles of MeOH), reaction time 30-40 min, catalyst (KOH) 1.5 % w/w.[19]

Xiangang Wang et. al Spray characteristics of biodiesels (from palm and cooked oil) and diesel under ultra-high injection pressures up to 300 MPa were studied experimentally and analytically. Injection delay, spray penetration, spray angle, spray projected area and spray volume were measured in a spray vessel using a high speed video camera. Air entrainment and atomization characteristics were analyzed with the quasi-steady jet theory and an atomization model respectively. The study shows that biodiesels give longer injection delay and spray tip penetration. Spray angle, projected area and volume of biodiesels are smaller than those of diesel fuel. The approximately linear relationship of non-dimensional spray tip penetration versus time suggests that the behavior of biodiesel and diesel sprays is similar to that of gaseous turbulent jets. The estimation on spray droplet size shows that biodiesels generate larger Sauter mean diameter due to higher viscosity and surface tension.[20]

Tareq A. Albahri et. al A theoretical model for predicting the surface tension of pure liquid compounds from their molecular structure was presented in this paper. A back propagation artificial neural network algorithm was used to select the appropriate functional groups and investigate their contribution to the surface tension property. The networks were used to probe the functional groups and determine the ones that have significant contributions to the overall surface tension property and arrive at the set of groups that can best represent the surface tension for about 560 substances. The results obtained were futher compared with other methods in the literature.[21]

A Srisaipet et. al Martin’s equation, $\Delta G = \Delta G_f + z\partial G$, was extended to cover vaporization free energy. The extended equation was further expanded in terms of enthalpy and entropy and then used to correlate vaporization enthalpy and enthalpy of transfer from solution to gas. Data available in the literatures was used to validate and support the speculations derived from the proposed equation.[22]

Payri R. et al The current work focuses on the study of the influence of pressure and temperature on three important thermodynamic properties: speed of sound, compressibility and density of common diesel fuels. The sample fuels studied were conventional diesel, Rape Methyl Ester and a fuel used especially for winter season. Speed of sound and densities have been determined experimentally. The third property, Bulk Modulus, has been calculated from the other two. Speed of sound measurements have been carried out in wide range of temperatures ($298< T/K < 343$) and pressures ($15 < p/MPa < 180$), which represent the typical values used in injection systems for diesel engines. The obtained results were listed, with an uncertainty of 0.3%.[23]

Maria Jorge Pratas et. al The pressure influence in fuel density has become particularly important with the increased use of modern common rail systems, where pressures can reach 250 MPa. Little attention has been given to high-pressure biodiesel densities To overcome this lack of information, in this work, new experimental measurements, from 283 to 333 K and from atmospheric pressure to 45 MPa, were performed for methyl laurate, methyl myristate, and methyl oleate, for methyl biodiesels from palm, soybean, and rapeseed oils, and for three binary and one ternary mixture of these oils. Following previous works, where the cubic-plus-association equation of state (CPA EoS) was shown to be the most appropriate model to be applied to biodiesel production and purification processes, the new high-pressure experimental data reported here were also successfully predicted with the CPA EoS, with a maximum deviation of 2.5%.[24]

Andrew M. Duncan et. al. This study focuses on the viscosity of biodiesel samples, fatty acid methyl esters (FAMEs), derived from soybean oil, soybean oil from Vistive soybeans, canola oil, recycled canola oil that has been used in cooking and frying, and coconut oil from 283.15 to 373.15 K and pressures up to 131 MPa. Petroleum-derived diesel (ultra-low sulfur, number 2 diesel) has also been investigated to compare to the biodiesel samples. The viscosity of the samples increases linearly with pressure until approximately 35 MPa, followed by a higher order response to pressure. The viscosity of the biodiesel samples with pressure can increase nearly 300% over the pressure range investigated over their respective ambient-pressure viscosity.[25]

2.2 SUMMARY OF LITERATURE REVIEW

The survey of papers shows that adequate amount of work has been done in the field of measurement of surface tension, viscosity and bulk modulus of compressibility of biodiesels. Various equipments such as drop shape analyser, tensiometer, viscometer, pycnometer, gas chromatography techniques , automatic density meter etc. have been used for the prediction of the above properties. Also, FAMEs compositions of various biodiesels such as karanja, jatropha, soybean, rapeseed, palm etc. were provided in the papers. The processes of biodiesel production were also covered. Mathematical models to predict the values of the mentioned properties could be developed on softwares such as MATLAB which would work on some required feeded data from the user. To evaluate the FAMEs composition of biodiesels , gas chromatography (GC) techniques were applied. Mostly to predict the values of mentioned properties, FAMEs composition of biodiesels was a must.

2.3 GAPS IDENTIFIED

After meticulously reviewing the various researches, certain gaps have been found which require further attention. Those identified gaps are:

- The prediction of the values of properties have not been measaured at much higher temperatures (due to equipments constraint) in relation to the working engine conditions.
- Accurate data is not available in the literature.
- Some methods used for estimating the the surface tension has flaws as the method gives equal weightage to every individual FAME present in the biodiesel which is not in the actual case as each FAME has different levels of attractive forces at the surface of the biodiesel.
- Biodiesel's property parachor still needs an in depth research.
- The sudden dip in the value of surface tension of FAME C18:1 and C18:2 from C18:0 value is not known.
- Adequate data is not available for the property of bulk modulus of biodiesels.

2.4 OBJECTIVE OF THE PRESENT WORK

From the survey of various papers, it is very much clear that some mathematical models to predict the values of surface tension, viscosity and bulk modulus of compressibility of biodiesels or even diesel fuels can be developed by using the knowledge of composition of fatty acid methyl esters (FAMEs) of the biodiesel fuels.

- The mathematical models to predict the surface tension of biodiesels can be developed by using the knowledge of composition of biodiesels (FAMEs), value of density, molecular weight of biodiesel, operating temperature , average number of carbon atoms of the biodiesel, average number of double bonds in the biodiesel, and surface tension values of individual FAMEs. In totality , it is possible to develop three mathematical models for estimation of value of surface tension of the biodiesels.

- To estimate the value of viscosity of biodiesels, a mathematical model can be developed which would require the knowledge of viscosity value of individual FAMEs.

- In case of prediction of bulk modulus of compressibility of biodiesels, the data required would be the speed of sound in individual FAMEs of biodiesel and the value of density of biodiesels.

- These mathematical models could be developed on softwares such as MATLAB. Further, these models seem to be appropriate and promise to give results within a close range when the results would be compared to measured values found experimentally. Also an error analysis can be done to further verify the data found by mathematical models.

CHAPTER 3

SYSTEMATIC DEVELOPMENT OF MATHEMATICAL MODELS ON MATLAB

3.1 MATHEMATICAL MODELS FOR PREDICTION OF SURFACE TENSION OF BIODIESELS

The physical property surface tension plays an important role in the process of atomization of fuels in the compression ignition engines. Better atomization and enhanced air-fuel mixing helps in proper and complete combustion of the fuels , thereby increasing engine efficiency and reducing the amount of emission of pollutants. Variation of feedstock leads to differences in physical properties such as surface tension, viscosity, density, bulk modulus of compressibility etc. Hence each of the biodiesels has its own atomization characteristics. Literature survey has shown that a higher value of surface tension makes the fuel's droplet formation more difficult which causes inefficient combustion and low power output.

There are various methods to estimate the surface tension of biodiesel fuels. In this work , three methods or rather models will be described and developed on MATLAB software. The first model will be based on the parachor method called as the' Macleod – Sudgen method'. The second model will be based on - the data of average number of carbon atoms of FAMEs in the biodiesel , average number of double bonds of FAMEs in the biodiesel and temperature. The final model, the third model depends on surface tension value of individual FAMEs of the biodiesel. These three models were developed and coded on MATLAB.

3.1.1 THE PARACHOR BASED MACLEOD-SUDGEN MODEL

The parachor based model is the most basic method for the computation of surface tension of biodiesels. The surface tensions of different biodiesels are predicted based on the fatty acid methyl ester composition of biodiesels in mass fractions and their respective parchor values. The parachor values are allocated to the group of atoms based on their linkage and composition. The unit of parachor is $\{[(\mathrm{mN/m})^{0.25}]\times\mathrm{mol}/cm^3\}$ [8]. The following table shows the parachor value of the individual FAMEs :

Table 2: Parachor values of different individual FAMEs [8]

FAMEs	Parachor value by Allen	Parachor value by Knotts
C8:0	NA	NA
C10:0	489	495
C12:0	567	574
C14:0	645	657
C16:0	723	737
C18:0	801	817
C18:1	879	806
C18:2	779	795
C18:3	768	782
C22:1	946	967

These parachor values of the FAMEs were calculated by Sudgen . An equation given by Sudgen was utilized to calculate the parachor value of individual FAMEs.

$$\sigma = [\mathrm{P}(\rho_l - \rho_v)]^4 \tag{1}$$

The mentioned equation is used for parachor value evaluation. The surface tension σ, the liquid density ρ_l and ρ_v the vapour density values were found out experimentally. The parachor values were assumed to be additive with respect to ring, atomic and bond structural components.

Table 3: Structural contribution / increment to parachor [5]

Group	Increment in parachor value	Group	Increment in parachor value
C	9.0	1-methylbutyl	211.7
H	15.5	1-ethylpropyl	209.5
H(in OH)	10.0	1,1-dimethylpropyl	207.5
H (in HN)	12.5	1,2-dimethylpropyl	207.
$CH_2 < 12$ carbons	40.0	1,1,2-trimethylpropyl	243.5
$CH_2 > 12$ carbons	40.3	Triple bond	40.6
1-methylethyl	133.3	Three member ring	12.5
1-methylpropyl	171.9	Four member ring	6.0
2-methylpropyl	173.3	Five member ring	3.0
1,1-dimethylethyl	170.4	Six member ring	0.8
C_6H_5	189.6	Seven member ring	4.0

Using these data, the parachor values of FAMEs are calculated. Now, determination of surface tension requires the knowledge of parachor value of the biodiesel. To calculate the parachor value of biodiesel, the mass fractions (Xi) of the FAMEs present in the biodiesel is required. Then mentioned equation is applied [8]:

$$P_{bdf} = \text{X(i)} \times P_{ch}\text{(i)}. \qquad (2)$$

Furthermore, the knowledge of density and molecular weight of the biodiesel is required . The surface tension (γ) can be calculated by using the following equation [8]:

$$\gamma = \left(\frac{P_{bdf} \times \rho}{\text{Mw}}\right)^{0.25} \qquad (3)$$

This method can be made to work as a mathematical model on MATLAB software as shown here:

```
disp('CALCULATION OF SURFACE TENSION OF BIODIESELS USING
MATHEMATICAL MODELS')
disp('MODEL-1 THE PARACHOR BASED MODEL')
BDF=input(' enter the biodiesel >  ','s');
composition_BDF = input('enter the mass fraction of
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1
in order > ');
pchallen=[0 489 567 645 723 801 879 779 768 946];
pchknotts=[0 495 574 657 737 817 806 795 782 967];
pchbdf1=0;
pchbdf2=0;
   for j=1:10;
pchbdf1=pchbdf1+composition_BDF(j)*pchallen(j)/100;
pchbdf2=pchbdf2+composition_BDF(j)*pchknotts(j)/100;
   end

   fprintf('parachor value of%s according to Allen\n >
',BDF)
   disp(pchbdf1)
   fprintf('parachor value of %s according to knotts >
',BDF)
   disp(pchbdf2)
   density=input('enter density of biodiesel in kg/m^3>
');
   molweight=input('enter molecular weight of biodiesel in
g/mol > ');
   st1=((pchbdf1*density/(molweight*0.001))^0.25);
   st2=((pchbdf2*density/(molweight*0.001))^0.25);
   fprintf('surface tension of %s according to Allen is %s
mN/m \n> ',BDF,st1)
   fprintf('surface tension of %s according to Knotts is
%s mN/m\n\n > ',BDF,st2)
```

The above code is comprised of two parts:

- One part computes the parachor value of the biodiesel
- The other part computes the surface tension value of the biodiesel by commanding the user to input the density and molecular weight of the biodiesel.

This model is the most basic model for computing the surface tension value of biodiesels and as a result deviates most from the actual value of data computed experimentally. This model is best validated for pure liquid compounds. Biodiesel being a mixture of compounds (FAMEs) cannot be the most viable option to be used in this model for its surface tension calculation.

The result window appears as shown below (calculated for karanja biodiesel) :

```
CALCULATION OF SURFACE TENSION OF BIODIESELS USING
MATHEMATICAL MODELS

MODEL-1 THE PARACHOR BASED MODEL

 enter the biodiesel >  karanja

enter the mass fraction of
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1
in order > [0 0 9.89 4.89 12.89 1.67 53.51 17.18 0
0]parachor value ofkaranja according to Allen

 >   798.3733

parachor value of karanja according to knotts >   765.4107

enter density of biodiesel in kg/m^3> 868.5

enter molecular weight of biodiesel in g/mol > 281.9

surface tension of karanja according to Allen is
3.960228e+01 mN/m

> surface tension of karanja according to Knotts is
3.918703e+01 mN/m
```

3.1.2 THE GIBBS FREE ENERGY MODEL

Compared to the previous parachor based model, the gibbs free energy model predicts the surface tension of biodiesel with much less deviation. Now, a compound that has a molecular structure of CH_3-$(CH_2)_z$-X , this molecule can be divided into three groups- CH_3, $(CH_2)_z$ and X. The gibbs free energy of transfer from the liquid form to gas form was deduced from the total sum of the free energies of all the contributing groups.

$$\Delta G = \Delta G_f + \Delta G_1 + \Delta G_2 + \ldots\ldots..\Delta G_z \qquad (4)$$

The free energies of methylene and methyl groups are mostly similar hence the equation simplifies to:

$$\Delta G = \Delta G_f + z\partial G \qquad (5)$$

This rule of gibbs free energy addition is applied to different physical phenomena such as vapour pressure of liquid, viscosity of FAME and biodiesel. There is a relationship between surface tension and free energy of interface interaction of a liquid compound at constant, pressure and composition [3]:

$$\gamma = (\partial G/\partial A)_{T,P,X(i)} \qquad (6)$$

From thermodynamics, we know that

$$\Delta G = \Delta H - T\Delta S \qquad (7)$$

This equation can be restated in the following form:

$$\gamma = (\Delta H_f / \Delta A) - (T\Delta S_f / \Delta A) + (z\partial H / \Delta A) - (z\partial TS / \Delta A) \qquad (8)$$

It can be now expressed as:

$$\gamma = a + bz + cT + dzT \qquad (9)$$

The above equation can now be used for surface tension estimation of saturated FAME.

To calculate the surface tension of unsaturated FAMEs , one more parameter is added – the total number of double bonds of the unsaturated FAME. Following is the equation:

$$\Delta G = \Delta G_f + z\partial G + m\Delta G \qquad (10)$$

$$\gamma = a + bz + cT + dzT + em + fmT \qquad (11)$$

The value of coeffiecients a, b, c, d, e and f can be calculated by meticulous survey of literature review. This equation(11) can now be applied for surface tension calculation of biodiesel. The modifications needed are : the average number of carbon atoms and the average number of double bonds of the biodiesel considering the biodiesel to be composed of a single FAME [3].

To calculate the average number of carbon atoms and double bonds in the biodiesel , following equations can be applied respectively:

$$Z_{avg} = \Sigma X(i) \times z(i) \tag{12}$$

$$M_{avg} = \Sigma X(i) \times m(i) \tag{13}$$

The final equation for surface tension calculation of biodiesel is as follows:

$$\gamma = 60.211 - 0.4307\times z_{avg} - 0.1125\times T + 0.00207\times z_{avg}\times T + 3.676\times m_{avg} - 0.0089\times m_{avg}\times T \tag{14}$$

The MATLAB code for predicting the surface tension based on gibbs free energy model is as follows:

```
fprintf('MODEL 2- GIBBS ENERGY MODEL \n\n')
   composition_BDF = input('enter the mass fraction of 
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1 in 
order > ')
   z_avg = 
0.01*(8*composition_BDF(1)+10*composition_BDF(2)+12*composition_
BDF(3)+14*composition_BDF(4)+16*composition_BDF(5)+18*compositio
n_BDF(6)+18*composition_BDF(7)+18*composition_BDF(8)+18*composit
ion_BDF(9)+22*composition_BDF(10))
   m_avg = 
(composition_BDF(7)*1+composition_BDF(8)*2+composition_BDF(9)*3+
composition_BDF(10)*1)*.01
   temperature=input('enter working temperature in celsius > ');
   temperature=temperature +273.15;

   % from literature survey surface tension of biodiesel is 
given by-
   st3=60.211-0.4307*z_avg-
0.1125*temperature+0.00207*z_avg*temperature+3.676*m_avg-
0.00893*m_avg*temperature;
   fprintf('surface tension of %s according to gibbs model is %s 
mN/m >', BDF ,st3);
```

The result of the code is as follows:

```
 MODEL 2- GIBBS ENERGY MODEL

enter the biodiesel karanja

enter the mass fraction of
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1
in order > [0 0 9.89 4.89 12.89 1.67 53.51 17.18 0 0]

average number of carbon atoms in the biodiesel  karanja
is > 1.695860e+01

 average number of double bonds in the biodiesel  karanja
is > 8.787000e-01

enter working temperature in celsius > 40

surface tension of  karanja according to gibbs model is
2.944335e+01 mN/m
```

This result when compared to the value produced by the parachor based model shows that this model predicts better results as the parachor model’s value was 31 N/m whereas gibbs model’s value is 29 N/m. The value found experimentally for karanja biodiesel is 24 N/m.

The next model the Dalton’s mass average model gives good results compared to parachor based model but not as better as the gibbs free energy model. The data required are the surface tension value of individual FAMEs of the biodiesel. This model is the simplest of all.

3.1.3 THE DALTON TYPE MASS AVERAGE MODEL

Prediction of surface tension of liquid mixtures such as biodiesel and other compounds can be calculated using the Dalton type mass average equation shown below [3]:

$$\gamma = \Sigma X(i) \times \gamma(i) \qquad (15)$$

The surface tension of individual FAME is derived from their parachor value as mentioned earlier. However, literature survey has shown that this model would mostly over-predict the surface tension values. This problem can be rectified by adding specific weight factors to every individual FAME. Doing that significantly increases the complexity of the method. But still, this method is far better compared to the parachor based model.

The MATLAB model for this method is as follows:

```
fprintf('MODEL 3- DALTON TYPE MASS AVERAGE EQUATION\n');
   fames_st=[25.40 26.30 27.20 27.90 28.40 29.00 22.80 
23.80 29.60 30.10];
   fprintf('Surface tension value of C8:0 FAME is 25.40 
mN/m \n');
   fprintf('Surface tension value of C10:0 FAME is 26.30 
mN/m \n');
   fprintf('Surface tension value of C12:0 FAME is 27.20 
mN/m \n');
   fprintf('Surface tension value of C14:0 FAME is 27.90 
mN/m \n');
   fprintf('Surface tension value of C16:0 FAME is 28.40 
mN/m \n');
   fprintf('Surface tension value of C18:0 FAME is 29.00 
mN/m \n');
   fprintf('Surface tension value of C18:1 FAME is 22.80 
mN/m \n');
   fprintf('Surface tension value of C18:2 FAME is 23.80 
mN/m \n');
   fprintf('Surface tension value of C18:3 FAME is 29.60 
mN/m \n');
   fprintf('Surface tension value of C22:0 FAME is 30.10 
mN/m \n');
   composition_BDF = input('enter the mass fraction of 
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1 
in order > ');
   st_4 = .01*(composition_BDF*fames_st');
   fprintf('Surface tension of %s according to Dalton 
model is > %s\n\n', BDF, st_4);
```

The values of surface tension of individual FAMEs written in the code were taken from the literature.

The result window is as follows:

```
MODEL 3- DALTON TYPE MASS AVERAGE EQUATION

enter the biodiesel > karanja

Surface tension value of C8:0 FAME is 25.40 mN/m

Surface tension value of C10:0 FAME is 26.30 mN/m

Surface tension value of C12:0 FAME is 27.20 mN/m

Surface tension value of C14:0 FAME is 27.90 mN/m

Surface tension value of C16:0 FAME is 28.40 mN/m

Surface tension value of C18:0 FAME is 29.00 mN/m

Surface tension value of C18:1 FAME is 22.80 mN/m

Surface tension value of C18:2 FAME is 23.80 mN/m

Surface tension value of C18:3 FAME is 29.60 mN/m

Surface tension value of C22:0 FAME is 30.10 mN/m

enter the mass fraction of
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1
in order > [0 0 9.89 4.89 12.89 1.67 53.51 17.18 0 0]

Surface tension of karanja according to Dalton model is >
2.448857e+01 mN/m
```

The result generated by this model for karanja biodiesel is 24 mN/m which is lesser than both the other models prediction but is far better than the parachor based model.

All the three models in actual practice predicted the surface tension value of karanja biodiesel (in this case) at temperatures of 40˚C as the FAMEs composition of karanja was corresponding to 40˚C. Also for the gibbs energy model, the temperature taken was 40˚C as mentioned in the code earlier. The other two properties' calculation i.e., the viscosity of biodiesel and the bulk modulus of compressibility of biodiesel will now be further discussed.

3.2 MATHEMATICAL MODEL FOR PREDICTION OF VISCOSITY OF BIODIESEL

One of the factors contributing significantly to the atomization of fuel in compression ignition engines is the property of viscosity of fuel. It is so because viscosity affects the atomization process of fuel during the initial stages of combustion. A higher value of viscosity causes interference in the fuel injector operation which results in poorer atomization in the fuel spray, which would eventually lead to injector problems such as sticking and thickening of oil on the rings, choking of injector and increase of carbon deposits on the walls of cylinder and piston.

A lower value of viscosity is recommended for biodiesels. Moreover, the conversion of vegetable oil to FAMEs of biodiesel results in significant reduction of viscosity (dynamic) value , usually from 40 – 60 mPas to directly in the range of 2 – 8 mPas which actually depends on the FAME composition of biodiesel. We know, biodiesel is a mixture of various fatty acid methyl esters , and further each FAME contributes to the overall viscosity of the biodiesel which makes it necessary to find a mathematical relation between the FAME composition and viscosity value of individual FAMEs. Hence the viscosity value of FAMEs and their mixtures in biodiesel can be useful for estimating the viscosity value of biodiesel [18].

The 'Grunberg – Nissan' method/model is well able to estimate the value of viscosity of liquid mixtures including biodiesels. This model requires knowledge of two parameters: the viscosity value of the individual FAMEs and the mass fractions of individual FAMEs in the biodiesel [18]. Now we see two limitations of this model: firstly the value of viscosity of the individual FAMEs must be known beforehand; the second limitation being that the structural information of the individual FAMEs such as the unsaturated bond features, the size of the FAME cannot be grasped by this model. Viscosity is such a kind of property which largely depends on the structure and length of fatty acids. Also, the longer the fatty acid hydrocarbon chain, the larger will be the value of viscosity of that particular FAME and the greater the number of unsaturated bonds, the lower the value of viscosity of that particular FAME.

The purpose of this model is to develop a simple method which would predict the viscosity value of the biodiesel using the knowledge of viscosity value of FAMEs and the mass fractions of individual FAMEs of the biodiesel.

The equation (Grunberg – Nissan equation) used is shown below [18]:

$$1n\ \mu_m = \Sigma X(i) \times \mu(i) + \Sigma\Sigma X(i) \times X(j) \times Gij \tag{16}$$

This equation was actually meant for binary liquid mixtures and was found to be a best fit equation for non – associated liquids. However, literature survey shows that this model could be extended beyond binary liquid mixture levels and even gave less value of errors 5 – 10 %. Also biodiesel being a mixture of non – associated liquids (the FAMEs) have similar structure of the FAMEs. This leads to almost no interaction between the components of the mixture which results in the value of the interaction parameter ‘Gij’ to be very small so that it could be neglected [18].

With this modification, the Grunberg – Nissan equation leads to the following form :

$$1n\ \mu_m = \Sigma X(i) \times \mu(i) \tag{17}$$

The values of viscosity of individual FAMEs and mass composition of various biodiesels were taken from the literature. The MATLAB code to predict the viscosity is as follows :

```
disp('PREDICTION OF VISCOSITY OF BIODIESELS USING
MATHEMATICAL MODEL')
   disp('GRUNBERG-NISSAN MODEL')
   BDF=input('Enter the biodiesel >','s')
   fprintf('Viscosity of C8:0 is 0.99 mPas\n')
   fprintf('Viscosity of C10:0 is 1.40 mPas\n')
   fprintf('Viscosity of C12:0 is 1.95 mPas\n')
   fprintf('Viscosity of C14:0 is 2.69 mPas\n')
   fprintf('Viscosity of C16:0 is 3.60 mPas\n')
   fprintf('Viscosity of C18:0 is 4.74 mPas\n')
   fprintf('Viscosity of C18:1 is 3.73 mPas\n')
   fprintf('Viscosity of C18:2 is 3.05 mPas\n')
   fprintf('Viscosity of C18:3 is 2.65 mPas\n')
```

```
   fprintf('Viscosity of C822:1 is 5.91 mPas\n')
   composition_BDF = input('enter the mass fraction of
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1
in order > ');
   viscosity=[0.99 1.40 1.95 2.69 3.60 4.74 3.73 3.05 2.65
5.91];
   composition_BDF=0.01*composition_BDF
   fames_viscosity=0.001*viscosity;
   log_viscosity=log(fames_viscosity);
   log_bdf_viscosity=composition_BDF*log_viscosity';
   bdf_viscosity=exp(log_bdf_viscosity);
   fprintf('Viscosity of %s is %s Pas \n', BDF,
bdf_viscosity);
```

The result window for karanja biodiesel is as follows:

```
PREDICTION OF VISCOSITY OF BIODIESELS USING MATHEMATICAL
MODEL

GRUNBERG-NISSAN MODEL

Enter the biodiesel > karanja

BDF =  ' karanja'

Viscosity of C8:0 is 0.99 mPas

Viscosity of C10:0 is 1.40 mPas

Viscosity of C12:0 is 1.95 mPas

Viscosity of C14:0 is 2.69 mPas

Viscosity of C16:0 is 3.60 mPas

Viscosity of C18:0 is 4.74 mPas

Viscosity of C18:1 is 3.73 mPas

Viscosity of C18:2 is 3.05 mPas
```

```
Viscosity of C18:3 is 2.65 mPas

Viscosity of C822:1 is 5.91 mPas

enter the mass fraction of
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1
in order > [0 0 9.89 4.89 12.89 1.67 53.51 17.18 0 0]

composition_BDF =         0         0    0.0989    0.0489
0.1289    0.0167    0.5351    0.1718         0         0

Viscosity of  karanja is 3.318305e-03 Pas
```

This result is well within the viscosity value range for karanja biodiesel as per the literature survey. Hence this model can well predict the value of viscosity of biodiesels.

3.3 MATHEMATICAL MODEL FOR PREDICTION OF BULK MODULUS OF COMPRESSIBILITY OF BIODIESELS

The bulk modulus of compressibility of fuels has a significant affect on the hydraulic behavior of fuels during the injection of fuel in the compression ignition engines. The fuel is subjected to very high pressures in the fuel injector and during injection. The bulk modulus of compressibility of fuels gives an insight about how much the fuel would reduce in volume . For small reductions in volume, this term is sometimes called as dilatation [15].

A higher value of bulk modulus of compressibility would mean rapid increase in pressure in the fuel injector and during injection which leads to earlier lift of needle in the pump line nozzle type fuel injection system. Hence this would imply an advance in injection timing which would eventually lead to knocking problems in the CI engines. As per the literature review, biodiesels in CI engines increases chances of more NOx emissions from the engine. Although in fuel injection systems such as the common rail injection system where a constant pressure is maintained at the injection pressure and the fuel is injected electromechanically rather hydraulically, the influence of bulk modulus of compressibility of fuels is not seen in such cases [15].

It has been stated that the fluids' compressibility at lower pressures is due to the consumption of free spaces between the loosely packed molecules. But at higher pressures, the compressibility gets significantly reduced as now the molecules of fuel itself gets compressed which would be obviously opposed by the inter molecular repulsive forces. This means the bulk modulus of compressibility should increase with increase in pressure simply because the resistance to compression increases as mentioned earlier.

A MATLAB model has been made for predicting the bulk modulus of biodiesels after doing a meticulous literature survey. The changes in bulk modulus of compressibility with fuel's FAME composition and molecular structure is an area of interest and that too particularly in the case of biodiesels, which may possess significantly different molecular structures than conventional diesel fuels. The bulk modulus of compressibility can be measured through observations of dilatation in fuels under pressure . Mathematically, the bulk modulus of compressibility can be estimated from measurements of the speed of sound in the fluids like FAMEs, because the insentropic bulk modulus is directly related to the speed of sound in a fluid as shown below:

$$\mathrm{Ks} = \rho \times U^2 \tag{18}$$

The speed of sound in various FAMEs can be calculated by using the Auerbach's model as mentioned:

$$\mathrm{U} = \left(\frac{\gamma}{6.33\times 10^{-10}\times\rho}\right)^{2/3} \tag{19}$$

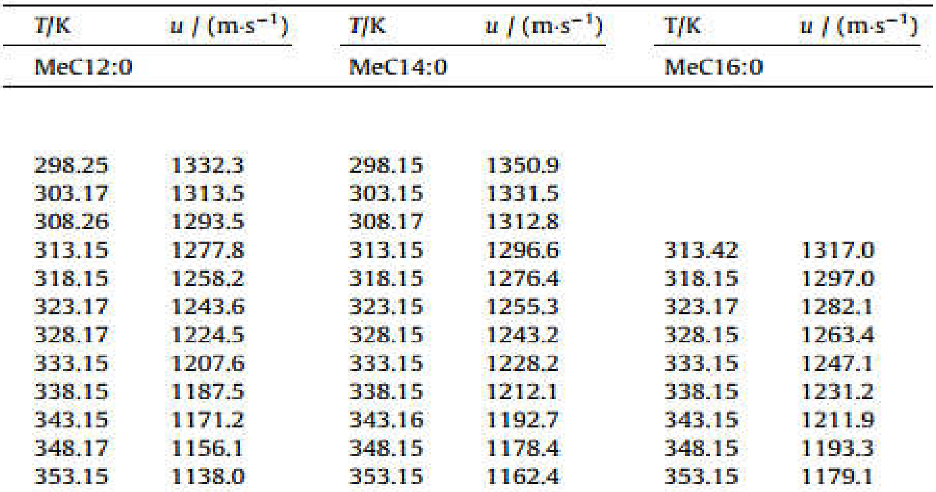
Calculating speed of sound in individual FAMEs through the above mentioned model can be very cumbersome as it include two parameters: surface tension and density of FAME. This can lead to significant error margins . Hence the speed value is taken from the experimental data given in literature [17]. The speeds are shown in the following table 4 and 5. The methyl esters used for experimentations were 98 % pure hence can be relied for measurement of speed calculation.

From the data of speed of sound in individual FAMEs , the speed of sound of sound in the required biodiesel can be calculated as follows [17]:

$$\mathrm{U_{BD}} = \Sigma \mathrm{X(i)} \times \mathrm{U(i)} \tag{20}$$

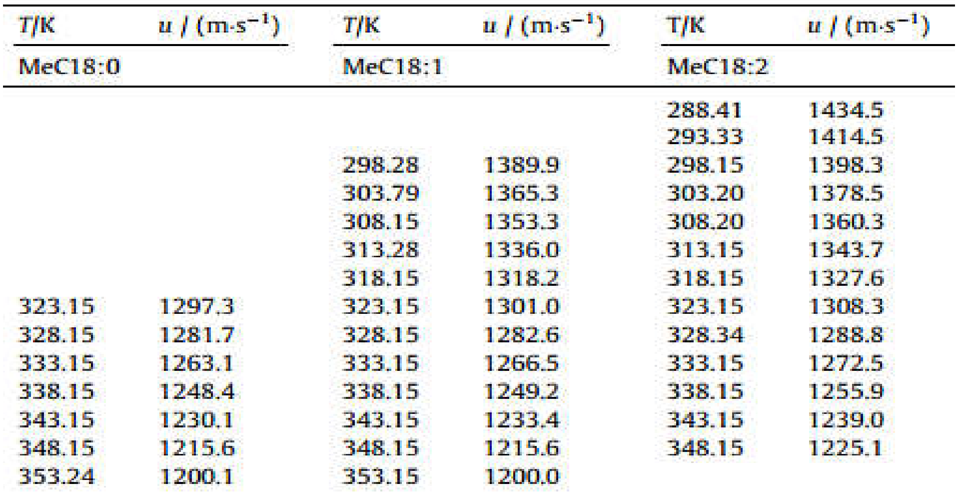
The composition of fatty acid methyl ester and the density of biodiesel needs to be known beforehand for calculation of bulk modulus of compressibility. A model can be easily coded on softwares such as MATLAB for calculation of bulk modulus . The following code shows the model on MATLAB software:

Table 4: Speed of sound in C12:0, C14:0, C16:0 FAMEs[17]



T/K	u / (m·s^{-1})	T/K	u / (m·s^{-1})	T/K	u / (m·s^{-1})
MeC12:0		MeC14:0		MeC16:0	
298.25	1332.3	298.15	1350.9		
303.17	1313.5	303.15	1331.5		
308.26	1293.5	308.17	1312.8		
313.15	1277.8	313.15	1296.6	313.42	1317.0
318.15	1258.2	318.15	1276.4	318.15	1297.0
323.17	1243.6	323.15	1255.3	323.17	1282.1
328.17	1224.5	328.15	1243.2	328.15	1263.4
333.15	1207.6	333.15	1228.2	333.15	1247.1
338.15	1187.5	338.15	1212.1	338.15	1231.2
343.15	1171.2	343.16	1192.7	343.15	1211.9
348.17	1156.1	348.15	1178.4	348.15	1193.3
353.15	1138.0	353.15	1162.4	353.15	1179.1

Table 5: Speed of sound in C18:0, C18:1, C18:2 FAMEs[17]



T/K	u / (m·s^{-1})	T/K	u / (m·s^{-1})	T/K	u / (m·s^{-1})
MeC18:0		MeC18:1		MeC18:2	
				288.41	1434.5
				293.33	1414.5
		298.28	1389.9	298.15	1398.3
		303.79	1365.3	303.20	1378.5
		308.15	1353.3	308.20	1360.3
		313.28	1336.0	313.15	1343.7
		318.15	1318.2	318.15	1327.6
323.15	1297.3	323.15	1301.0	323.15	1308.3
328.15	1281.7	328.15	1282.6	328.34	1288.8
333.15	1263.1	333.15	1266.5	333.15	1272.5
338.15	1248.4	338.15	1249.2	338.15	1255.9
343.15	1230.1	343.15	1233.4	343.15	1239.0
348.15	1215.6	348.15	1215.6	348.15	1225.1
353.24	1200.1	353.15	1200.0		

The speed of sound in FAMEs such as C8:0, C10:0, C18:3 and C22:1 were calculated as per the Auerbach model.

```
fprintf('PREDICTION OF BULK MODULUS OF COMPRESSIBILITY OF
BIODIESELS')
   biodzl=input('enter the biodiesel > ', 's');
   density_bdf=input('enter the density of biodiesel in
kg/m3 > ')
   sos_fame=[0 0 1335.9 1334.0 1332.1 1328.3 1326.4 1338.8
1340.0 0];
   composition_BDF = input('enter the mass fraction of
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1
in order > ');
   sos_bdf=sos_fame*composition_BDF';
   fprintf('speed of sound in %s is %m/s',
biodzl,sos_bdf);
   bulk_modulus=density_bdf*(sos_bdf^2);
   fprintf('bulk modulus of %s is %s > ',biodzl,
bulk_modulus);
```

The result window for karanja biodiesel is as follows:

```
PREDICTION OF BULK MODULUS OF COMPRESSIBILITY OF
BIODIESELS

enter the biodiesel > karanja

enter the density of biodiesel in kg/m3 > 868.5

density_bdf =  868.5000

enter the mass fraction of
C8:0,C10:0,C12:0,C14:0,C16:0,C18:0,C18:1,C18:2,C18:3,C22:1
in order > [0 0 9.89 4.89 12.89 1.67 53.51 17.18 0 0]

speed of sound in karanja is 1.331006e+03 m/s

bulk modulus of karanja is > 1.538614e+09 Pa
```

The result above shows that the speed of sound in karanja biodiesel is 1331 m/s whereas the bulk modulus of compressibility of karanja biodiesel is 1538 MPa which is in accordance with the data trends in the literature .

3.4 EXPERIMENTAL PROCEDURE FOR DETERMINATION OF SURFACE TENSION OF BIODIESEL

The measurement of surface tension of biodiesel and other fuels is done by using a Nima Dynamic surface tensiometer. It is a sophisticated computer controlled equipment which evaluates and documents the forces that biodiesel exerts to counteract the external forces induced due to the immersion of the Platinum / Iridium Du Nouy ring in the sample (biodiesel) to be measured. This technique is also known as Pull – Force method [6].

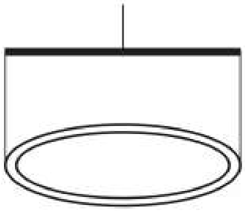


Figure 1: Ring of the Du Nouy Ring Tensiometer [6]

The surface tension is measured by using the following equation :

$$P_t = P_r + \gamma_{ideal} \times 4\pi R \tag{21}$$

Figure 2: Du Nuoy Ring Tensiometer [6]

The final surface tension will be given by the following equation :

$$\gamma = f \times \gamma_{ideal} \tag{22}$$

3.5 EXPERIMENTAL PROCDURE FOR DETERMINATION OF VISCOSITY OF BIODIESEL

Viscosity can be measured by using Automatic Viscosity meter commonly called as Viscobath. This equipment measures viscosity in terms of time (seconds). 40˚C was chosen as the temperature for measuring the viscosity as per the standards. The fuel is taken and filled into the capillary. The capillary is now placed in the viscobath. The stopwatch is then started when the meniscus reaches the upper mark and stopped when the meniscius reaches the lower mark. The time recorded in seconds is then multiplied with the constant of capillary tube. By using the following equation , the kinematic viscosity of the fuel sample can be calculated:

$$\upsilon = k \times t \tag{23}$$

Plate 3: Viscometer

The capillary tube used in the viscometer is shown below. The tube is usually made of glass.

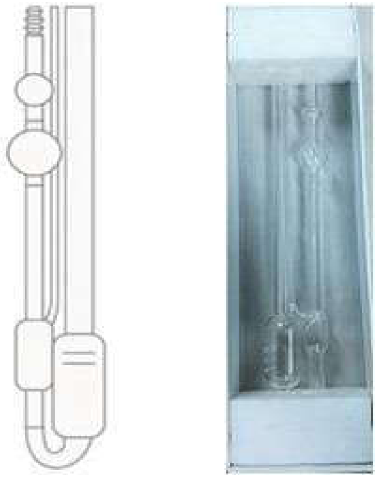


Figure 4: Capillary tube used in Viscosity measurement

The principle used for measuring the kinematic viscosity of the sample is the capillary action of the capillary tube which sucks the fluid up due to pressure difference. The temperature is controlled at 40°C for single grade oils and at 40°C and 100°C for for multi – grade oils. The relation between time and kinematic viscosity is used to determine the required parameter. Samples having more value of viscosity will take more time to flow through the capillary tube and vice versa. Capillary tubes made of glass are most commonly used.

Viscometer gives the value of the kinematic viscosity of the sample. The dynamic viscosity of the sample can be calculated by multiplying the density of biodiesel to the kinematic viscosity value of the sample.

$$\mu = \rho \times \upsilon \tag{24}$$

3.6 EXPERIMENTAL PROCEDURE FOR DETERMINATION OF BULK MODULUS OF COMPRESSIBILITY OF BIODIESEL

The measurement techniques used for measuring the bulk modulus of compressibility of biodiesels consists of an instrument which can measure the reduction in the volume of the liquid sample when the sample is exposed to higher pressures at isothermal conditions . This can be done by using high pressure jerguson gauge that can handle pressures of upto 33 MPa [15],[16].

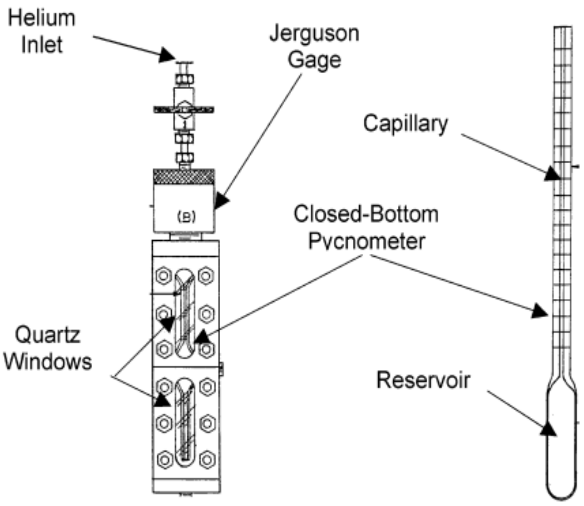


Figure 5: High pressure housing for bulk modulus measurement showing Jerguson gauge and Pycnometer [15]

Plate 6: Thermal bath with high pressure test chamber [16]

Now, the bulk modulus is calculated by measuring the change in height within the pycnometer tube as the pressure inside the pressure cell (jerguson gauge) is varied. Here distilled water is used as a calibration standard.

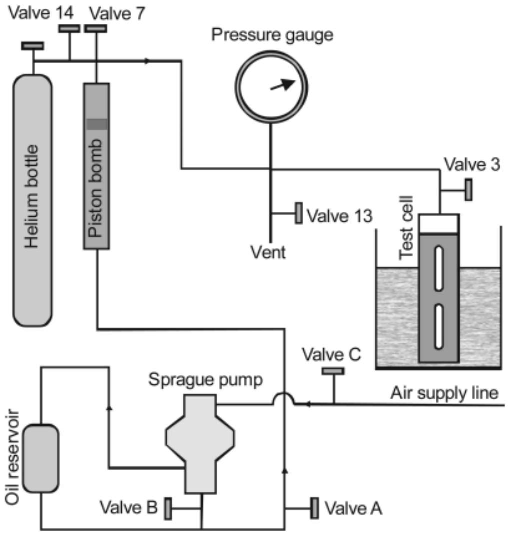


Figure 7: layout of experimental installation [16]

The figure above shows the experimental setup of the measurement equipments used for bulk modulus of compressibility measurement of fuels. The pressure cell (pycnometer) is connected to the high pressure line via a swage – lock. First of all, the pressurized oil in the oil reservoir needs to be purged. For that, the valve C is opened keeping the valve A closed and the valve B open and the Sprague pump is turned on. The valve B is turned off as soon as the oil starts to flow . The helium stored in the helium cylinder is now allowed into the pressure cell by opening valve 14 and then valve 7. Then valve 14 is closed to save the helium. The pump is used to achieve high pressures which can be turned on and by opening valve C ,closing valve B and opening valve A , the pressurized oil can be allowed to flow into the piston bomb. Now once an desired volume is achieved in the pycnometer, valve C is closed and the readings are taken [16].

The tangent bulk modulus can then be calculated by applying the following formula:

$$K_s = -\frac{V_i + V_{i-1}}{2}\frac{P_i - P_{i-1}}{V_i - V_{i-1}} \tag{25}$$

CHAPTER 4

RESULTS AND DISCUSSION

In this section of the thesis, results derived from the various MATLAB models for the calculation of the values of the properties of surface tension, viscosity and bulk modulus of the biodiesels are presented. The error in the values predicted will also be discussed by comparing the predicted data with the data found experimentally. A total of six biodiesels have been dealt with for these analyses. The biodiesels taken into consideration for the mentioned analyses are –

- Karanja
- Jatropha
- Soybean
- Palm
- Sunflower
- Rapeseed

4.1 Surface Tension prediction by the Parachor Based model

The parachor based model for surface tension prediction requires the values of three properties of biodiesels namely : the parachor value; the density of biodiesel and the molecular weight of biodiesel . The graph below compares the parachor value (according to Allen and Knotts), molecular weight and density of the above mentioned six biodiesels to give a better understanding about the factors which influence the surface tension. Parachor values for the individual FAMEs were given by Allen and Knotts and both the values differ in a significant manner.

Graph below compares the parachor values (according to Allen and Knotts), molecular weight and density of the mentioned biodiesels.

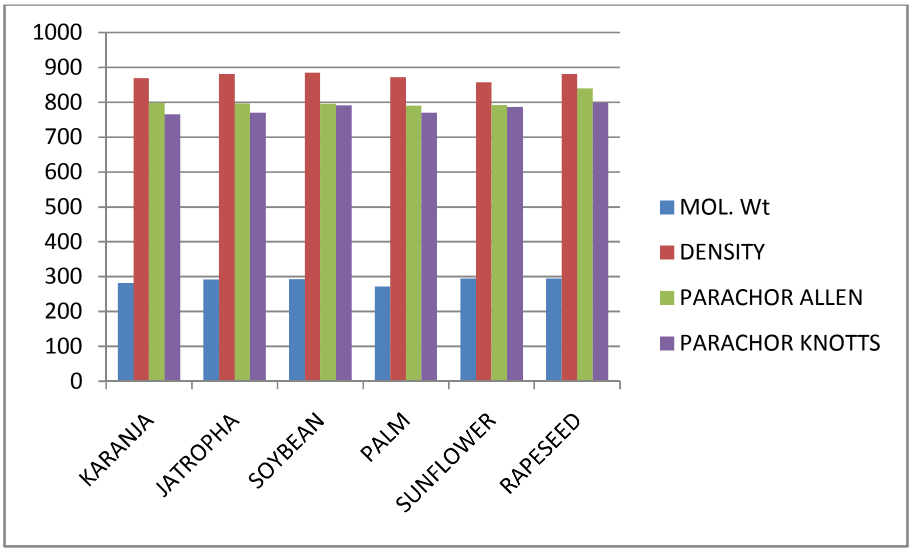


Figure 8: Comparison of various properties of biodiesel

As can be seen from the graphs , all of the six biodiesels have similar value of properties which simply implies that the value of surface tension calculated by the parachor based models would be close to each other. The graph below shows the value of surface tension calculated by Parachor model (according to Allen's and Knotts' parachors) :

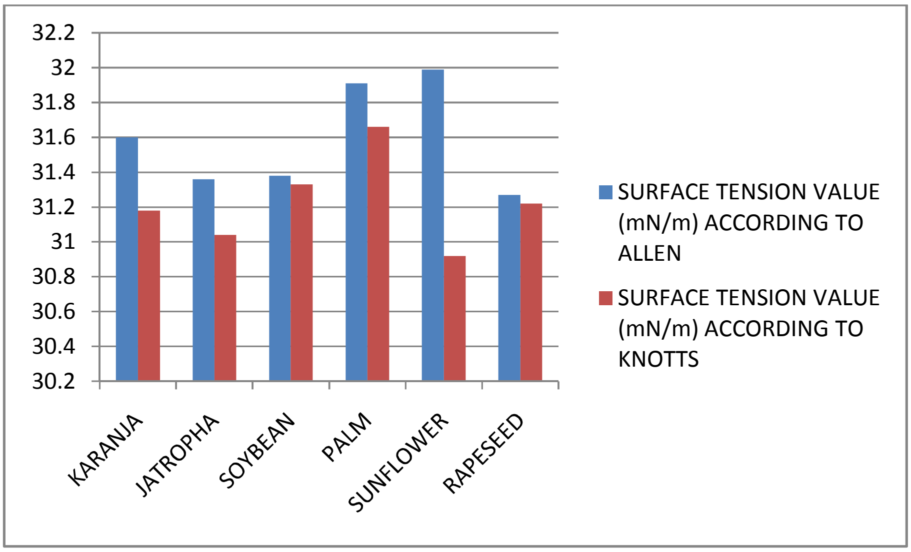


Figure 9: Predicted value of surface tension by Parachor model

Following table shows the measured values of the surface tension of six biodiesels:

Table 6: Measured values of Surface tension of biodiesels

Biodiesel	Surface tension in milliNewton/metre γ_{exp} (mN/m)
Karanja	28.62
Jatropha	30.10
Soybean	28.20
Palm	28.50
Sunflower	28.37
Rapeseed	29.39

Now, the error analysis for the surface tension values is done by comparing the predicted values and the experimental values and the percentage error is calculated.

Table 7: Error analysis for the Parachor Based model (allen parachors')

Biodiesel	$\gamma_{predicted}$ (mN/m) (By Allen Parachor)	Error = $\gamma_{predicted} - \gamma_{exp}$	% Error
Karanja	31.60	2.98	10.41
Jatropha	31.36	1.26	4.18
Soybean	31.38	3.18	11.27
Palm	31.91	3.41	12.01
Sunflower	31.99	2.62	9.23
Rapeseed	31.27	1.88	6.39

Table 8: Error analysis for the Parachor Based model (Knotts parachors')

Biodiesel	$\gamma_{predicted}$ (mN/m) (By Allen Parachor)	Error = $\gamma_{predicted} - \gamma_{exp}$	% Error
Karanja	31.18	2.56	8.9

Jatropha	31.04	0.94	3.12
Soybean	31.33	3.13	11.09
Palm	31.66	3.16	11.08
Sunflower	30.92	2.55	8.98
Rapeseed	31.22	1.83	6.22

Graph below shows the surface tension value of the biodiesels measured experimentally and calculated by the parachor model using Allen's parachor value and Knotts' parachor value

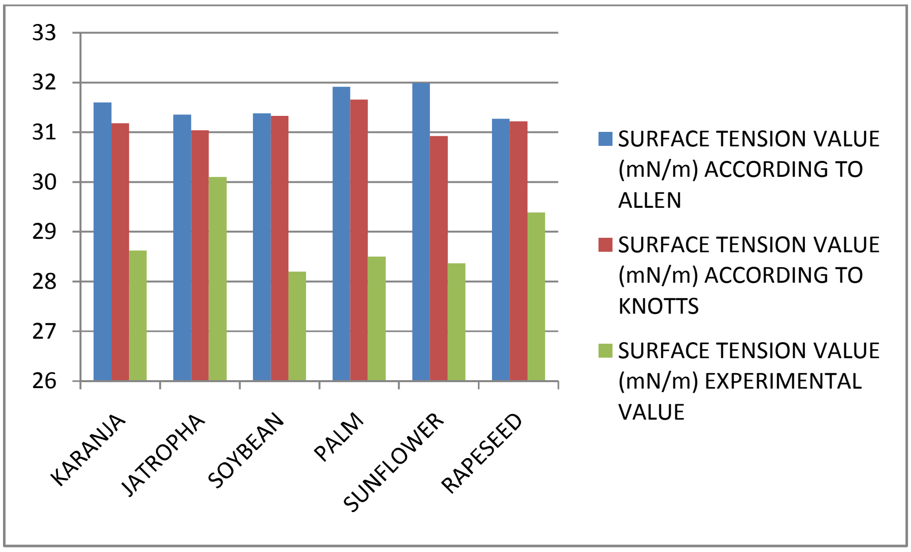


Figure 10: Surface tension calculated vs Surface tension found experimentally

4.2 Surface tension prediction by Gibbs free energy model

The surface tension prediction by the gibbs model requires the knowledge of parameters such as : the average number of carbon atoms of the FAMEs of which the biodiesel is composed of , the average number of double bonds of the FAMEs of which the biodiesel is composed of ,the working temperature value and the FAMEs composition of the biodiesel in mass fraction. Table below shows the average number of carbon atoms and the average number of double bonds of the biodiesel which could then explain any biodiesel to be a single fatty acid methyl ester which would take the value of carbon atoms as the value of average number of carbon atoms of the FAMEs of the biodiesel and the number of double bonds as the average number of double bonds of the FAMEs of the biodiesel.

Table 9: Average number of carbon atoms and double bonds of the biodiesel

Biodiesel	Avg number of C atoms	Avg no of double bonds
Karanja	16.95	0.87
Jatropha	17.20	1.1
Soybean	17.80	1.56
Palm	17.12	0.59
Sunflower	17.68	1.52
Rapeseed	17.89	1.3

Table above can now be understood as if the biodiesel is composed is itself a single fatty acid methyl ester having above values as number of carbon atoms and double bonds . Hence this method simplifies the complexity of the FAMEs composition of the biodiesel and appears to be a better model. The next table shows the surface tension value of the six biodiesels at a temperature of 40°C. Surface tension values for other temperatures can also be calculated by this model.

Table 10: Predicted values of Surface tension by Gibbs model at 40℃

Biodiesel	γ_{calc}(mN/m)
Karanja	29.44
Jatropha	29.69
Soybean	30.22
Palm	29.19
Sunflower	30.17
Rapeseed	30.02

Graph below shows the variation of surface tension of karanja, jatropha and soybean with temperature.

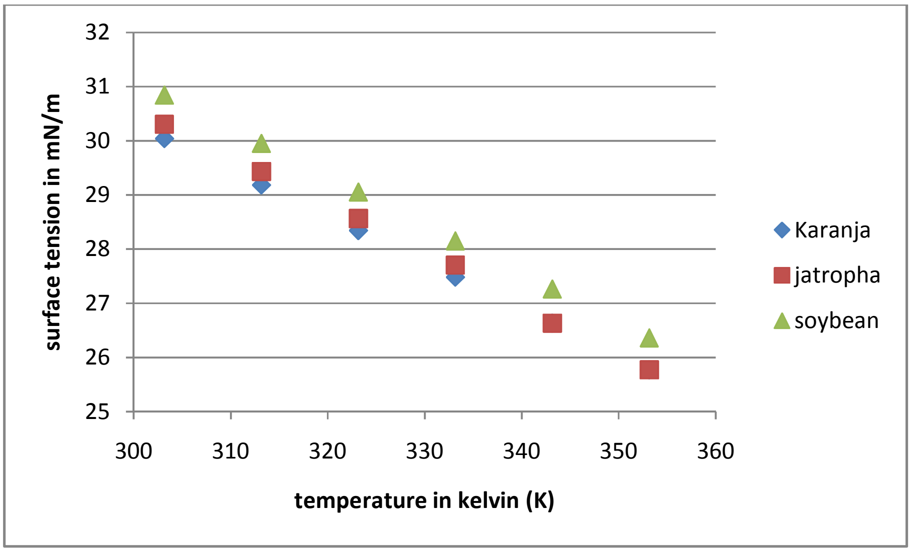


Figure 11: Variation of surface tension of karanja, jatropha and soybean with temperature

The next graph shows the results for palm, sunflower and rapeseed.

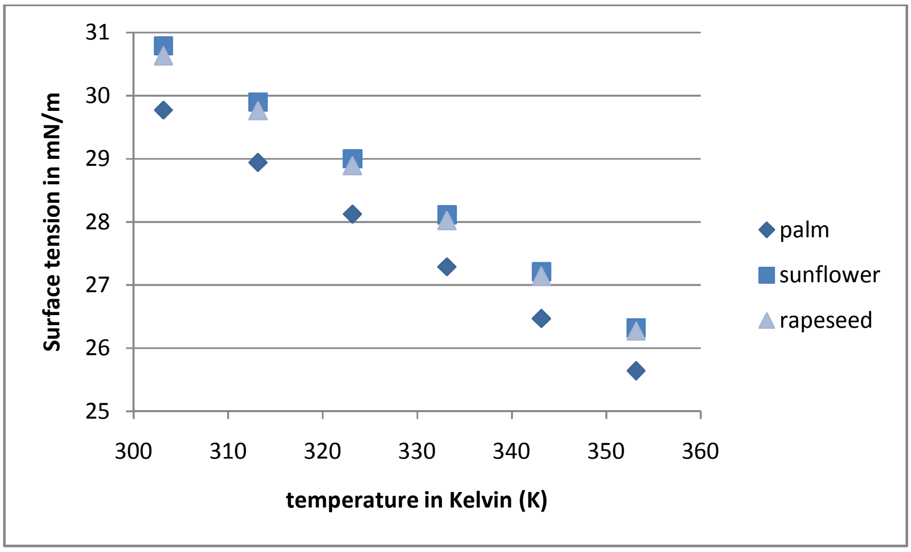


Figure 12: Variation of surface tension of palm, sunflower and rapeseed with temperature

Table 11: Error analysis for the Gibbs Energy model (at 313K)

Biodiesel	$\gamma_{predicted}$ **(mN/m)**	**Error =** $\gamma_{predicted} - \gamma_{exp}$	**% Error**
Karanja	29.44	0.82	2.8
Jatropha	29.69	-0.41	1.3
Soybean	30.22	2.02	7.1
Palm	29.19	0.69	2.4
Sunflower	30.17	1.8	6.3
Rapeseed	30.02	0.63	1.8

Comparing the data with the parachor based model , the error associated with this model is relatively low and can be preferred over the previous parachor based model.

4.3 Surface tension prediction by Dalton type mass average model

The surface tension prediction by the Dalton type mass average model requires the knowledge of parameters such as: the individual surface tension values of FAMEs and the FAMEs composition of the biodiesel. The values of surface tension of individual FAMEs were found experimentally though can also be calculated using the parachor equation. Experiment data are the most accurate data eventually hence has been taken as the reference in this case. The surface tension data for the six biodiesels predicted by this model is shown in the table below:

Table 12: Surface tension prediction at 40℃

Biodiesel	$\gamma_{predicted}$ **(mN/m)**
Karanja	24.48
Jatropha	25.58
Soybean	24.77
Palm	25.79
Sunflower	23.84
Rapeseed	25.05

Graph below shows clearly the difference between the calculated surface tension value and the experimentally measured value.

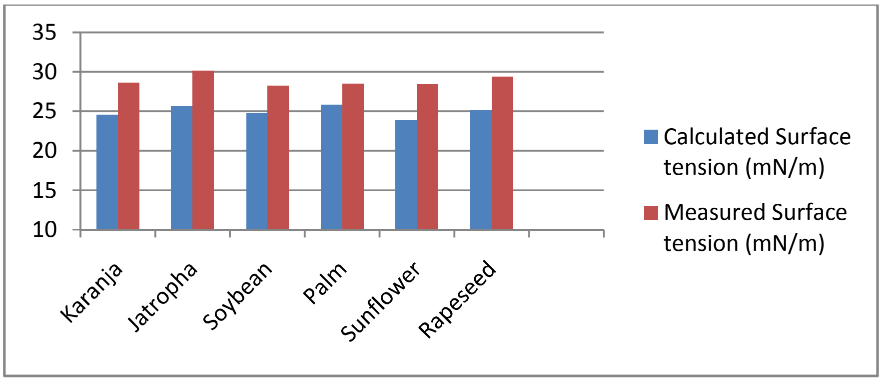


Figure 13: Surface tension by Dalton model

Table 13: Error analysis for the Dalton type mass average model (at 313K)

Biodiesel	$\gamma_{predicted}$ **(mN/m)**	**Error =** $\gamma_{predicted} - \gamma_{exp}$	**% Error**
Karanja	24.48	-4.14	14.46
Jatropha	25.58	-4.52	15.01
Soybean	24.77	-3.43	12.16
Palm	25.79	-2.71	9.52
Sunflower	23.84	-4.34	15.61
Rapeseed	25.05	-4.53	14.76

Seeing the error values of this model, it can be cocluded that this model is least suited for surface tension prediction compared to other two models, the best model being the Gibbs free energy model.

4.4 Viscosity prediction by the Grunberg – Nissan model

Viscosity prediction by this model requires knowledge of the viscosity values of individual FAMEs of which the biodiesel is composed of and the individual FAMEs composition of biodiesel in mass fraction. The viscosities of the six biodiesels were predicted and then compared with the experimental values. The values of the viscosities of the individual FAMEs have been taken from the literature which are the experimental values. A good prediction value is made by this model .

The table below shows the predicted value, experimental value and their comparison showing errors :

Table 14: Error analysis for the Nissan Grunberg model (at 313K)

Biodiesel	$\upsilon_{predicted}$ **(mPas)**	υ_{exp} **(mPas)**	**Error =** $\gamma_{predicted} - \gamma_{exp}$	**% Error**
Karanja	4.31	4.33	-0.02	0.46
Jatropha	4.11	4.18	-0.07	1.6
Soybean	3.27	3.26	0.01	0.31
Palm	3.59	3.59	0.0	0
Sunflower	3.49	3.52	-0.03	0.85
Rapeseed	3.48	3.72	-0.24	6.45

Graph below shows clearly that the model predicts the values of viscosity very close to the actual values found experimentally.

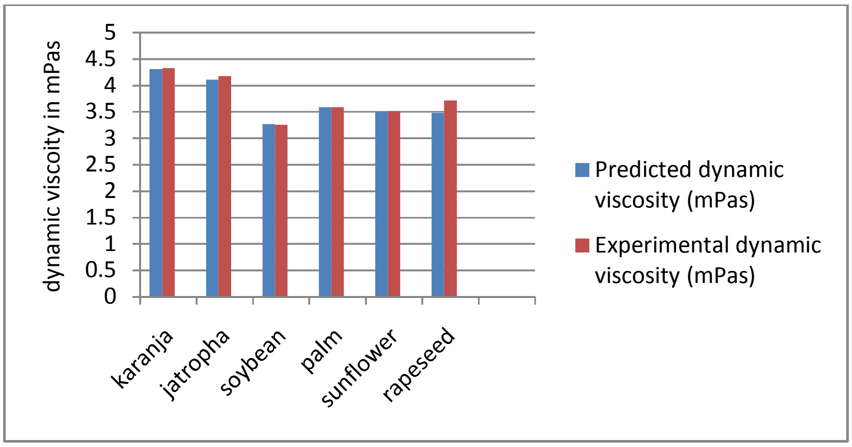


Figure 14: Viscosity values comparison graphically

4.5 Bulk modulus of compressibility prediction by MATLAB model

The bulk modulus of compressibility of biodiesels can be predicted by using the knowledge of speed of sound in biodiesels and the density of the biodiesel. To calculate the speed of sound in the biodiesel, the speed of sound in the individual FAMEs of which the biodiesel is composed of needs to be known. The values of speed of sound in the FAMEs can be calculated using the Aeurbach's model. In this thesis, those values have been taken from literature.

Table below shows the values of bulk modulus of compressibility of the mentioned six biodiesels:

Table 15: Values of bulk modulus of compressibility of biodiesels

Biodiesel	Predicted K_s (MPa)
Karanja	1538
Jatropha	1475
Soybean	1576
Palm	1537
Sunflower	1491
Rapeseed	1558

The experimental values of the bulk modulus of compressibility of biodiesels is not given in the literature hence cannot be analysed for comparison. But still, these values comply with the ranges for the values of bulk modulus of compressibility of fuels.

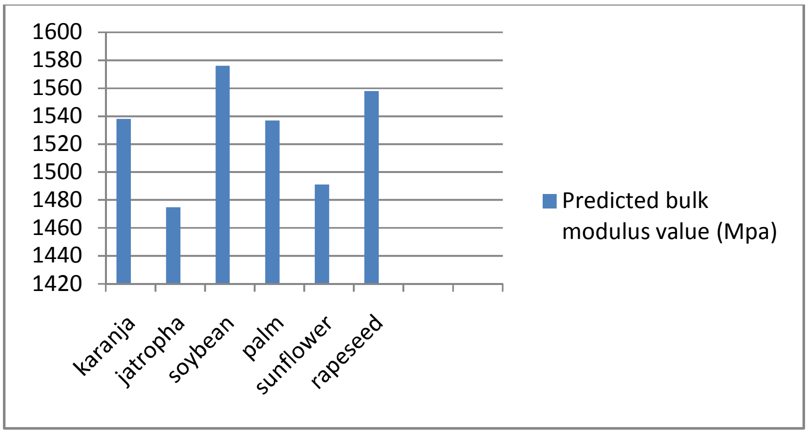


Figure 15: Comparison of bulk modulus of biodiesels graphically

CHAPTER 5

CONCLUSION AND FUTURE RECOMMENDATIONS

5.1 Conclusion

The three mathematical models made on MATLAB for predicting surface tension values, one mathematical model for predicting viscosity values and one mathematical model for predicting bulk modulus of compressibility of biodiesels showed good results when compared to the values of the mentioned properties found experimentally.

- The Gibbs free energy model proved to be the best fit model for predicting the surface tension as the error in values were relatively lower compared to the other two models with a maximum error of 7.1% and minimum error of 1.3%. Also only this model could show the variation of surface tension values with the changes in temperature. This feature is important as surface tension relies heavily on temperature.

- The Nissan-Grunberg model estimates viscosity values accurately with maximum error of 6.45% and minimum error of 0%.

- The bulk modulus of compressibility model estimated the values of biodiesels within the specified ranges of values for it as per literature survey.

  The advantage of the proposed models is that these models work on the physical properties of the biodiesels which are well defined and are related to the thermodynamic parameters, which makes it easy for further refinement of the relations used in these models.

5.2 Future recommendations

From this study of the prediction of the values of surface tension, viscosity and bulk modulus of compressibility of biodiesels using MATLAB software, it is found that the models developed had some shortcomings which need more aspects to be found :

- The variation of parachor values of biodiesels with temperature is still unknown. Temperature plays a major role in change of surface tension value and since surface tension relies on parachor values as per the parachor based model , there has to be a definite correlation (thermodynamic) between temperature and parachor.

- The parachor based model and the Dalton type average mass model for predicting surface tension value could predict the value at a temperature of 40℃ only which is a major drawback.

- More Study on variation of bulk modulus of compressibility of biodiesels with temperature needs to be done.

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