B.TECH. PROJECT REPORT

On

Ignitability of Biofuels

By

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DISCIPLINE OF MECHANICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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IGNITABILIY OF BIO-FUELS

PROJECT REPORT

Submitted in partial fulfillment of the
Requirements for the award of the degree

Of

BACHELOR OF TECHNOLOGY

In

MECHANICAL ENGINEERING

Submitted by:

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May 2022

CANDIDATE'S DECLARATION

We hereby declare that the project entitled **"Ignitability of Bio-Fuels"** submitted in partial fulfillment for the award of the degree of Bachelor of Technology in '**Mechanical Engineering**' completed under the supervision of **Dr. Ankur Miglani, Assistant Professor, Discipline of Mechanical Engineering, IIT Indore** is an authentic work.

Further, we declare that we have not submitted this work for the award of any other degree elsewhere.

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PREFACE

This report on **"Ignitability of Bio-Fuels"** is prepared under the guidance of

Dr. Ankur Miglani.

Through this report, we have attempted to study the ignitability of fuels by different Thermal Gravimetric Analysis. We have put the main efforts in finding the most accurate model available for calculating the activation energy of different fuels that we have used. This report also describes benefits of the biofuels and their blends and how they can be used as viable replacement of conventional fuels.

Through this thesis, efforts have been made to present the methodology, results, and conclusions of the study in a lucid and comprehensive manner. Graphs, tables, Figures have been included to make the content more illustrative.

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Without their support this report would not have been possible.

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ABSTRACT

The aim of this bachelor thesis is to explore unconventional fuels by studying their ignitability. The depletion of non-renewable energy sources has accelerated the need to look for renewable energy sources. Biofuels have shown encouraging characteristics in terms of clean energy and availability. The ignitibility is studied with respect to activation energy (Ea.). There are very few research papers analyzing the activation energy (Ea.) of such fuels and even fewer describing the ignitability. The similar fuels are grouped together, and results are compared with each other. We take samples of different fuels and study Thermal Gravimetric Analysis (TGA). Designate a suitable method to assess the Ea. and then implement it on TGA graphs. The conclusion reports the Ea. of different fuels and discusses insights on different patterns of Ea. of different fuel groups. We observe that the biodiesels have lower activation energy compared to their oils. The addition of halloysite slightly increases the activation energy of biomass but the additive is considered beneficial for the overall health of the boiler and furnace. The future work includes the study of different aspects of ignitability such as flame temperature, heat release rate, flash point, etc.

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CHAPTER 1

Introduction

1.1 Historical Background
1.2 What are biofuels?
1.3 Problem definition
1.4 Structure of Document

The excess use of conventional energy sources such as coal, petrol, and diesel has led to a dangerous level of pollution and drastic climate changes. Moreover, these fuels are non-renewable, and a big part of our economy relies on power production from conventional fuels. The need to find more efficient, less polluting, and renewable fuels is escalating steadily.

1.1 Historical Background

Solid biofuels have been used since the discovery of the fire. Wood is the earliest form of biofuel used by the ancient people for cooking and heating. With the discovery of electricity, man discovered another way to use biofuels. Biofuels have been used for a long time to generate electricity. This form of fuel was discovered even before the discovery of fossil fuels, but with the discovery of fossil fuels such as gas, coal and oil, the production and use of biofuels has been severely affected. Rudolf Diesel was the guy who invented diesel engine in 1890s. This engine could run on different fuels including vegetable oils. Since petroleum fuels were cheap no one was interested in finding the alternative. In early 1930s, there was keen interest in splitting fatty acids from glycerin to create thinner product as diesel. Process goes by and successfully tested on several engines. In World War II, due to shortage of petroleum fuels vegetable oils were used instead. As time goes by, biofuels are getting more and more popular and are keen interest of scientists including India, US, Austria, South Africa. As the fossil fuels are declining slowly causing hazards to the environment, we need to meet up the ever-increasing demand for energy and for fulfilling this thing constant shortage of fuel attracted the attention of the various academics and governments to the issues of energy crisis and the use of biofuels. The twentieth century came with the attention of the people towards the use of biofuels. Some of the main reasons for the people shifting their interest to biofuels were the rising prices of oil, emission of the greenhouse gases and interest like rural development. So here we come up with biofuels which are derived from biomass.

1.2 What are biofuels?

Biofuels are combustible fuels created from biomass like food crops, oilseeds, wood, algae, animal fat, etc. Crop residual, vegetable oils, and wood are common sources of biomass from which our samples are derived. They are formed by variety of process and some of the process we will be going to discuss in this report. They are renewable, economical and the use of Bio-fuels results in a reduction of Green House Gases emissions. Additionally, biofuels (like biodiesel and ethanol) can be a potential replacement for conventional fuels since it does not require any additional machinery to operate and can work on conventional machines and engines with approximately same efficiency producing negligible environmental hazards.

1.3 Problem definition

This project is based on the various kinetic models that different people have given to study the ignitability of this biofuel. The parameter here we will be focusing on is average activation energy. Various models and methods have been presented by various scientist based on different kind of assumptions and environmental conditions.

Our first objective here is to study the Thermal Gravimetric Analysis and different kinds of kinetic models and find the most efficient model of all so that we can calculate the activation energy of various fuels.

Our second objective here is to comment upon the ignitability of the various fuels and how does blending effect, synergic effect, and other chemical property change and physical property change affect their ignitability based on their average activation energy that we will calculate using above model.

1.4 Structure of the document

This report is organized in 2 different parts with 5 chapters with first part consist of study of various models and finding the optimum model among them and second part consist of applying that model to find the activation energy of the samples that we are going to use

Chapter 2 focuses on thermal analysis using Thermal Gravimetric Analysis and study of kinetic analytic approach to find out activation energy of the give fuel. Here we will also find out the best analytical method for finding activation energy

The subsequent chapters consist of our test fuels on which all TGA process will be conducted, and model will be applied. We have organized into four categories, based on their base fuel, as –

Chapter 3 Cereal Straw – Samples with halloysite additive and without additive
Chapter 4 Oils – Samples of Peanut Oil, Canola Oil, and their Biodiesel and
Chapter 5 Bitumen Coal and Pine Sawdust Blend
Chapter 6 Wood – Untreated wood, Heat-Treated wood, Impregnated wood and Impregnated as well as Heat-Treated wood

We will evaluate the activation energy (Ea.) of each biofuel and compare the results within the same category and combinations. Then we researched further to find the reasons behind different observations in **conclusions and discussions.**

CHAPTER 2

Methods and Models

2.1 Thermal Gravimetric Analysis
2.2 Methods and different Models
2.3 Kissinger's Method Application

Thermal analysis is a technique which is used to study the temperature and time during heating or cooling which causes physical change. Every approach is defined and applied based on the physical change which is going to be analyzed. Depending upon the purpose, it's very crucial to use different techniques or combination of multiple techniques while evaluating material characteristics. Several methods have been given in the chart given below.

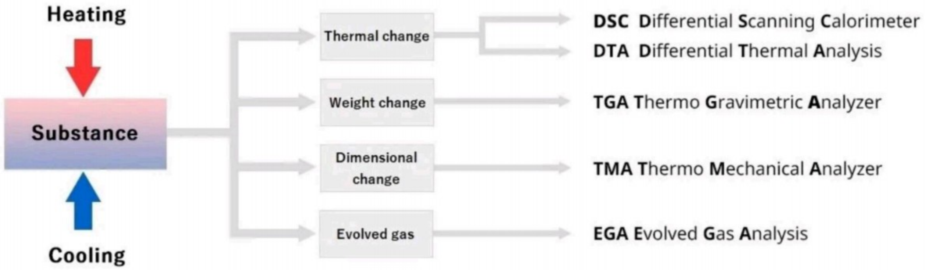


Figure 2.1 Available techniques for Thermal Analysis

Here we will study the mass weight change parameter with respect to time/temperature so here we will be employing TGA (Thermal Gravimetric Analysis) method for our purpose.

2.1 Thermal Gravimetric Analysis

It is a technique in which mass or weight of the sample is recorded as a function of controlled temperature or time. This phenomenon is used for qualitative as well as quantitative analysis. It can measure things like mass/weight loss by heating, melting point, heat and energy transitions, etc.,

For instance, loss in the mass due to H_2O present with the reactants., and this H_2O may be because of adsorption or water of crystallization. For example, loss of H_2O due to water of crystallization is,

$$CuSO_4.5H_2O \rightarrow CuSO_4.H_2O + 4H_2O$$

The instrument used in this technique is thermobalance. Using this thermobalance and recording the change in mass /weight with respect to temperature we will get a curve called thermograph or TGA curve.

Alternatively, data can be presented as a derivative thermogravimetric (DTG) curve, which is a plot of the rate of change of mass with respect to time or temperature. against time or temperature. TGA curve and DTG curve for a mass sample is shown below.

In the below graphs the curve that is on left of Y-axis left is our TGA curve which represents mass lost with respect to temperature and the curve on right of Y-axis represents the DTG curve which is nothing but the differential curve of TGA curve. The DTG curve is negative since we are having mass loss as temperature increases.

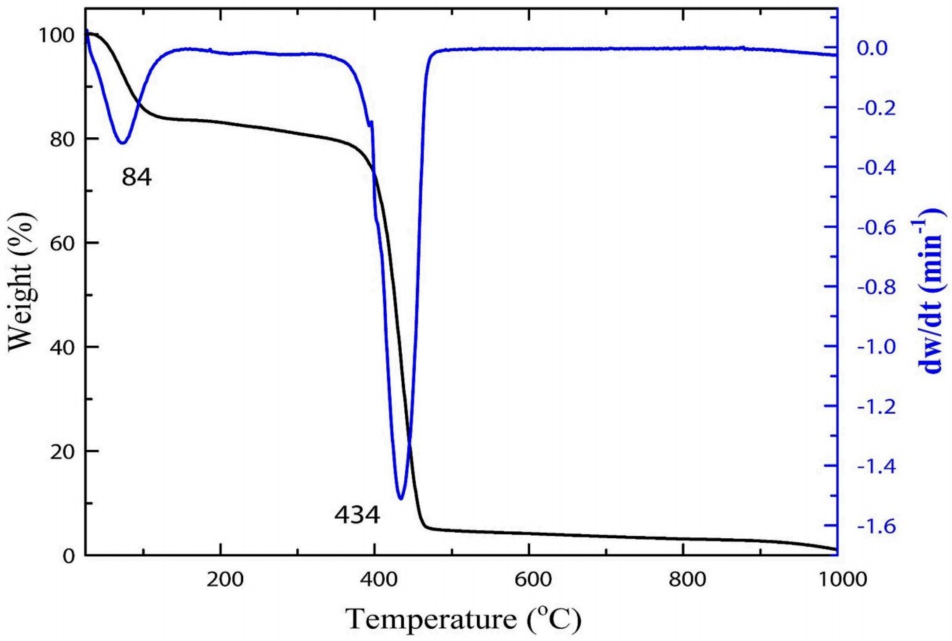


Figure 2.2 General DTG and TGA Curve

2.2 Methods and different Models

For studying the decomposition and thermal stability of various components TGA has received increasing attention within the last decade. Here we will use this technique to study the ignitability of various kind of bio – fuels. And we will employ various kinetic models to comment upon the ignitability based on activation energy we have obtained using the most efficient model available.

Together with much criticism regarding its use within the determination of rate constants; activation energies; reaction orders and Arrhenius pre-exponential constants. The values obtained depend on atmosphere; sample mass; sample shape; flow rate; heating rate but also on the mathematical treatment accustomed evaluate the info. the info obtained by TGA are studied employing a type of techniques. within the kinetic methods, the subsequent symbols are usual.

- Ea.: apparent activation energy (kJ/mol),
- A: pre-exponential factor (min^{-1}),
- n: apparent order of reaction,
- R: universal gas constant (8.3136 J/K mol),
- T: temperature (Kelvin),
- α: degree of conversion or fractional mass loss,
- t: time (min),
- β: heating rate (°C/min), and
- k: rate constant (s^{-1}).
- $\frac{d\alpha}{dt}$: rate of reaction
- $f(\alpha)$: Reaction model

For all kinetic studies basic rate equation at constant temperature:

$$\frac{d\alpha}{dt} = k.f(\alpha) - (1)$$

Now it is assumed that reaction model $f(\alpha)$ is proportional to the concentration of the material it will react with:

$$f(\alpha) = (1-\alpha)^n - (2)$$

Also, the rate constant k is determined through the Arrhenius equation:

$$k = A.e^{-\frac{E_a}{R.T}}$$

The combination of the previous equations gives the following:

$$\frac{d\alpha}{dt} = A(1-\alpha)^n . e^{-\frac{E_a}{R.T}} - (3)$$

Introducing the heating rate, β into Eq. (3), we have:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} . e^{-\frac{E_a}{R.T}} . dt - (4)$$

Above expression (4) we have obtained is the fundamental expression of analytical methods to calculate kinetic parameters based on TGA data on different environments and assumptions.

Now we will be looking at the different available analytical methods to evaluate activation energy as shown in Table 2.1

Table 2.1 Various Analytical Methods

Method	**Expression**	**Plots**	**Consideration**
Kissinger	$\frac{d(\ln(\beta/Tm^2))}{d(1/Tm)} = \frac{-Ea}{R}$	$ln\left(\frac{\beta}{T_m^2}\right)$ Against $\frac{1}{T_m}$	The product $n(1-\alpha)_m^{n-1}$ is independent of β and very nearly equal to 1 for first order reaction
Friedman	$ln\left(\frac{d\alpha}{dt}\right) = lnA + nln(1-\alpha) - \frac{Ea}{RT}$	ln(dα/dt) against 1/T for a constant α. $\frac{E}{R.T_0}$ against (1-α)	Comparison of mass loss rates (dα/dt) for a fractional mass loss, α, determined using different heating rates
Horowitz-Metzger	$ln\left[ln\left(\frac{1}{1-\alpha}\right)\right] = \left(\frac{Ea.\theta}{R.\mathrm{Ts}^2}\right)$	$ln\left(ln\left(\frac{1}{1-\alpha}\right)\right)$ Against θ	T_s; temperature at which $\frac{1}{1-\alpha} = \frac{1}{exp} = 0.368;$ θ=T-Ts. First – order kinetics
Flynn and Wall	$\frac{-dlog(\beta)}{d\left(\frac{1}{T}\right)} = 0.457.\frac{Ea}{R}$	d(logβ) against d(1/T)	Several curves at different heating rates
Ozawa Method	$logF(\alpha) = log\left(\frac{A.Ea}{R}\right) - log\beta - 2.315 - 0.4567\frac{Ea}{R.T}$	logβ against 1/T for a fixed degree of conversion	A, $(1-\alpha)^n$ and E are independent of T while A and Ea. Are independent of α
Van Krevelen	$\left[ln\left(\frac{1}{1-\alpha}\right) - 1\right] = ln\left[\frac{A}{\beta}.\left(\frac{0.368}{Tm}\right)^{\left(\frac{Ea}{R.T}\right)}.\frac{1}{\frac{Ea}{R.Tm}+1}\right] + \left(\frac{Ea}{R.Tm}+1\right).lnT$	ln(1/(1-α)) against ln T	At a fixed temperature, Tm, a maximum rate can be measured
Kamal	$ln\left[\frac{\frac{d\alpha}{dt}}{\alpha^{(2-n)}.(1-\alpha)^n}\right] = lnA - \frac{Ea}{R.T}$	$ln\left[\frac{\frac{d\alpha}{dt}}{[\alpha(2-n).(1-\alpha).n]}\right]$ Against 1/T	$f(\alpha) = \alpha^m.(1-\alpha)^n$

Several methods are mentioned above. First, our purpose here is to find the best model from all these available models based on different assumptions, environment conditions, order of the reaction, etc.,

Now looking at the first model which is Kissinger's Model. Here the method is taking the following things into consideration:

- Kissinger's method gives a single activation energy which is consistent with the assumption of single-step kinetics.
- It's a model-free non-iso-conversional method since it assumes constant activation energy throughout.
- In this model, the maximum reaction rate $(\frac{d\alpha}{dt})$ occurs with an increase in the reaction temperature. The degree of conversion (α) at the peak temperature (T_m) the DTG curve is a constant at different heating rates (β).

Here we will use this method for our purpose partly due to the reasons and assumptions mentioned above and because in other methods the activation energy does not come that accurate as we get from the Kissinger reason being other method involve complex mechanism like in Friedmann's method it involves calculation at different heating rates (β), for different conversion ratio's (α) the activation energy comes out to be different. And with this result we cannot comment upon the activation energy of the given fuel. Similarly, we do not have idea of the order of the reaction since for some models it's a prerequisite. Overcoming all these problem, Kissinger's model us provide activation energy since it assumes that order of the reaction is independent of reaction rate (β) and is nearly of order one and it assumes constant activation energy throughout.

2.3 Kissinger's Model Application

Above, we have discussed why Kissinger's Model is best suited for our purpose as per our understanding. This is also suited due to the availability of the data and experimentation done on this model.

We have discussed why we are using Kissinger's Model here. Now we will be applying this method to find out the activation energy so that we can comment upon the ignitability of the fuel.

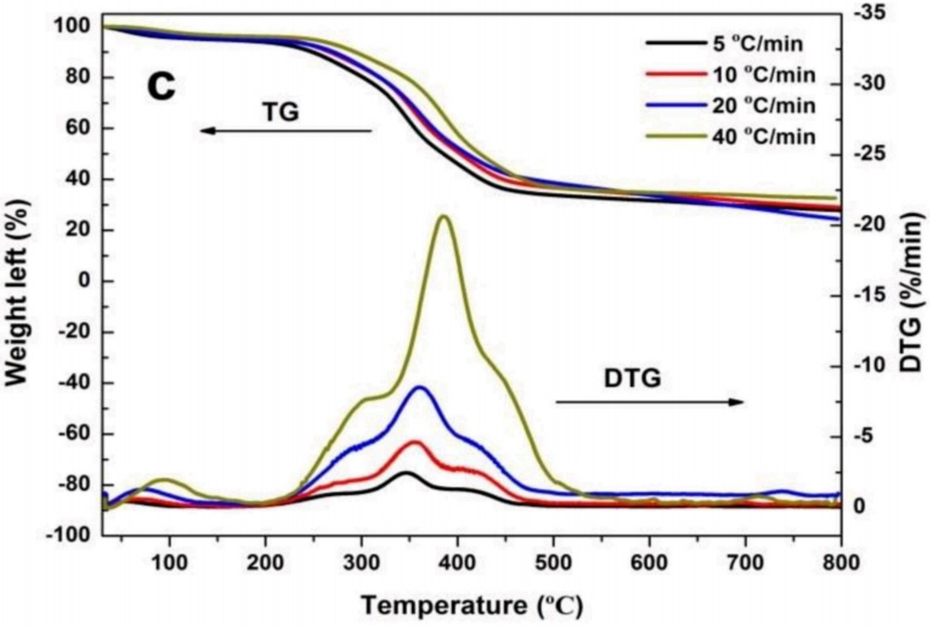


Figure 2.3 DTG Curve at different heating rates

Above, we can see the DTG and TGA curve for different heating rates that we will get as we will perform experiment and record the mass loss with respect to controlled temperature change. The experiments are conducted at different heating rates. For instance, here we have done experiment at four different heating rates as 5 °C/min, 10 °C/min, 20 °C/min, 40 °C/min. Since DTG curve is differential curve of TGA curve, its Y-axis gives the rate of reaction ($\frac{d\alpha}{dt}$). Now at the point where the rate of reaction is maximum is the place where maximum mass loss is occurring and hence will be the point where maximum of the energy is required. These are the peak points of the curve and hence temperature corresponding to them is peak temperature (T_m). The expression for Kissinger's Model from Table 2.1 is:

Expression: We will plot a graph of $\ln(\beta/T_m^2)$ versus $1/T_m$

$$\frac{d\left(ln(\beta/T_m^2)\right)}{d(1/T_m)} = -\frac{E_a}{R.T}$$

We will evaluate the activation energy for each peak and then add them up to give final activation energy for whole. Now as from figure 2.3 we can see 2 peaks lies there, first one is around 100 °C and second peak lies around 350 – 400 °C. Firstly, we will note the temperature (T_m) for each heating rate for every peak. Now with this temperature we will plot the graphs for different peaks and find the slopes of each as given in the expression. Adding up all the activation energies will provide us the value of total average activation energy from which we can comment on the ignitability of our fuels.

We will see the application of this model as we will use this model in subsequent chapters to study the ignitability of different kind of fuels including Canola Oil/ Peanut Oil Biodiesel, Wood with Heat Treatment, 90HC10PS and Cereal Straw.

CHAPTER 3

Cereal Straw

3.1 Materials and Combinations
3.2 Graphs and Methods
3.3 Result

Cereal straw is the crop residual of edible grains or seeds like Wheat, rice, corn, etc. Blending of halloysite with several types of biomasses has shown an increase in ash softening temperature. So, this additive can be used to reduce slagging and fouling in boilers. The formation of partially fused or molten deposits on walls of boiler or convection surfaces is called Slagging. The deposits formation on convection heat surfaces like superheaters and reheaters is called Fouling. Halloysite is an aluminosilicate with the empirical formula $Al2Si2O5(OH)4$. It can inhibit corrosion due to chlorine and the formation of low melting corrosive deposits during the combustion of biomass.

3.1 Materials and Combinations

We have two types of samples of it - with and without halloysite additive. The samples of biomass are marked as, DS0 —cereal straw without additive and DS4 – cereal straw with the halloysite additive. A sample of about 200 g of fuel was crushed and sieved to obtain particle size distribution defined as 100% < 200 μm. The sample fuel was divided into two parts, one was kept raw while the other was added up by 4 % of halloysite by weight. Then, prepared samples were mixed to procure optimum homogenization. A heating rate of 5 ◦C/min was used to heat the samples from ambient temperature (25 ◦C) to 105 ◦C. Samples were then held at 105 ◦C for 10 min to complete the moisture vaporization. Now, samples were heated up to 900 ◦C at different heating rates (5, 10, 15, 20 ◦C/min) to study the ignitability and held at the final treatment temperature for 10 min to complete the burnout process. Using TGA graphs and Kissinger method we evaluate the activation energy.

3.2 Graphs and Methods

Below given are the DTG graphs for DS0 and DS4. We will apply Kissinger's model on these curve as discussed in chapter 2 and find out their activation energy.

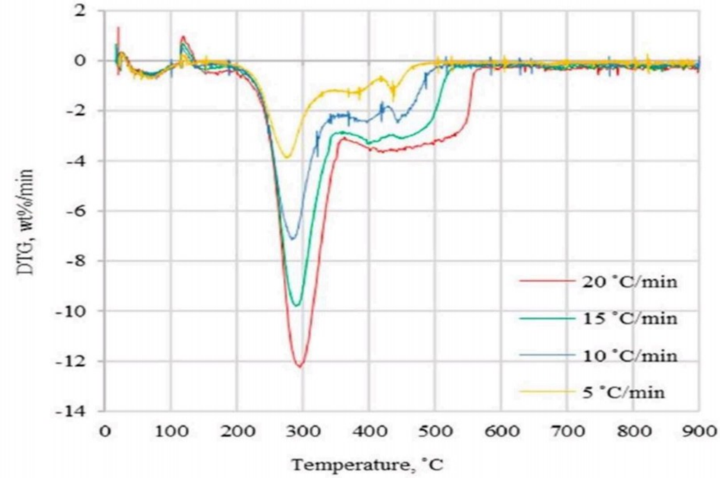


Figure 3.1(a). DTG curves for DS0 at different heating rates

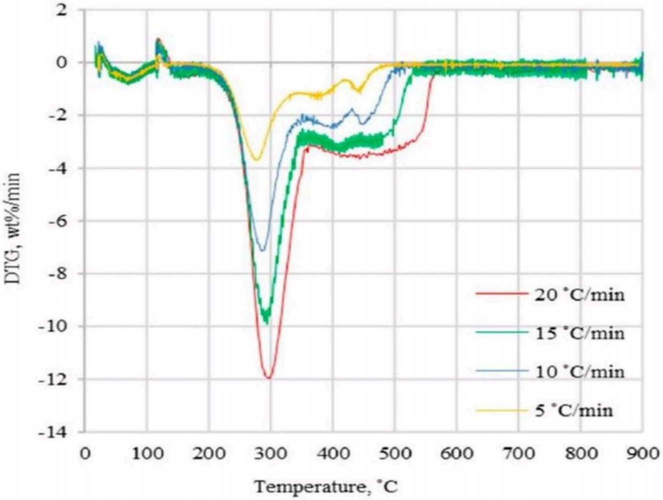


Figure 3.1(b) DTG curves for DS4 at different heating rates

3.3 Results

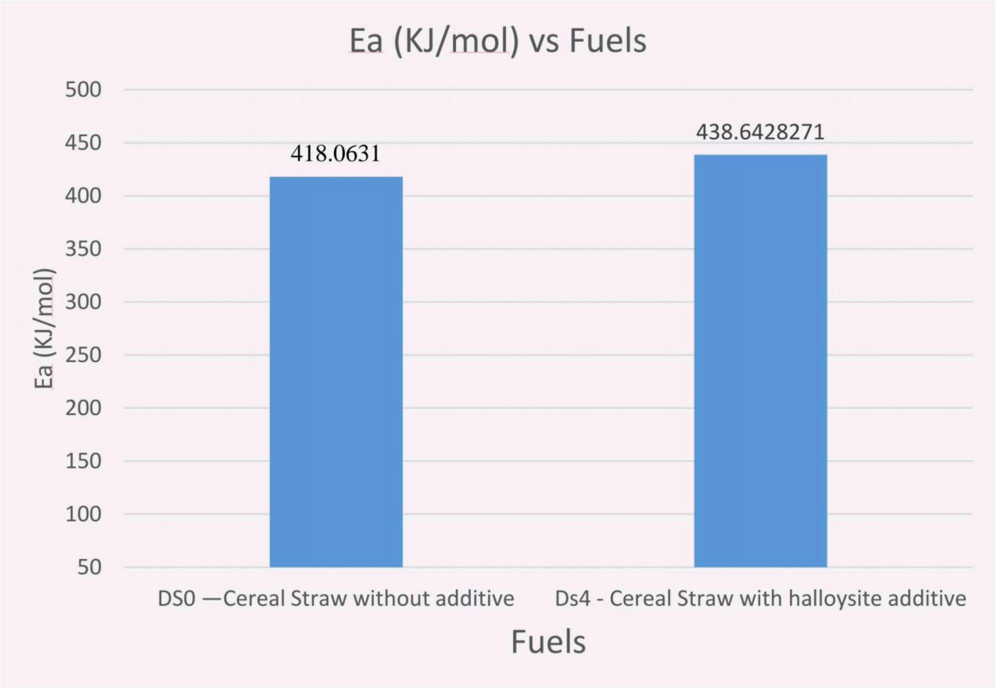


Figure 3.2 Comparison of Ea. Of DS0 and DS4

We see that the activation energy of biomass with halloysite additive is slightly more than the sample without additive.

CHAPTER 4

Canola Oil, Peanut Oil, and their Biodiesels

4.1 Materials and Combinations
4.2 Graphs and Methods
4.3 Results

4.1 Materials and Combinations

Biodiesel

Biodiesel is a cleaner-burning viable replacement for conventional fuel, made up of simple alkyl esters of fatty acids such as methyl and ethyl esters. It's a non-flammable, non-toxic, environment friendly energy source. This fuel is part of the family of biofuels and is produced from a biological resource called biomass like vegetable oils and/or animal oils/fats.

Biodiesel is obtained by a process called transesterification occurred by the reaction between an alcohol and an ester lipid in the presence of a catalyst (acidic, basic, or enzymatic) which create an ester (biodiesel) and a glycerin as a by-product. The final goal of this mechanism is to lower the viscosity of oil, as the physical characteristics of fatty acid methyl esters are close to those of diesel properties. We can see the reaction mechanism in the figure below

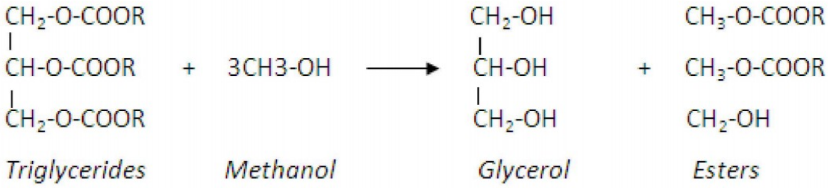
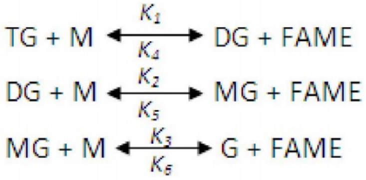


Figure 4.1 General Reaction mechanism of Transesterification

The above reaction mechanism comprise of three consecutive reversible reactions in which triglycerides gets converted to diglycerides; diglycerides get converted to monoglycerides followed by conversion of monoglycerides to glycerol as shown the reaction steps below. At every step an ester is formed, and three ester molecules are formed from one triglyceride molecule.



TG is triglyceride,
DG is Di glyceride,
MG is monoglyceride.

Figure 4.2 Formation of TG, DG, MG

In the preparation of biodiesel, standard method is to dissolve 1% catalyst (KOH) in alcohol (methanol or ethanol) with 1:6 oil alcohol molar ratio. The reaction is stirred at room temperature for approximately 30 minutes so that decatenation can occur. Now after decantation process, the by-product glycerin is removed and biodiesel is purified by wash water, biodiesel is dried and characterized.

Different type of feedstock oil can be used to prepare biodiesel. Here we will be using canola oil and peanut oil as feedstock oil. Obtaining this, Pure biodiesel, and its blends with diesel; B5, B10, B15, B20 are analyzed by using thermogravimetry.

Canola Oil

Canola oil is a kind edible fat extracted from a spread of rapeseed that's low in erucic acid, as opposition rape oil. The word ―canola was derived from ―Canadian oil, low acid. It comprises of 12% of total oil seed production as in 2006 and production has increased over the years.

Canola biodiesel is far more environment-friendly than petroleum (fossil diesel) since it lowers gas emissions by up to 90% and not having a catastrophic effect if spilled. These fuels also are not carcinogenic. Precisely, biodiesel reduces releases of CO, particulate, and sulphates yet as hydrocarbon and toxic air pollutant

What's good for the health is additionally good for the engine because of vegetable oil's low saturated fat content and hence canola oil is one in every of the foremost potent and efficient feedstock bases for biodiesel with excellent cold-flow properties.

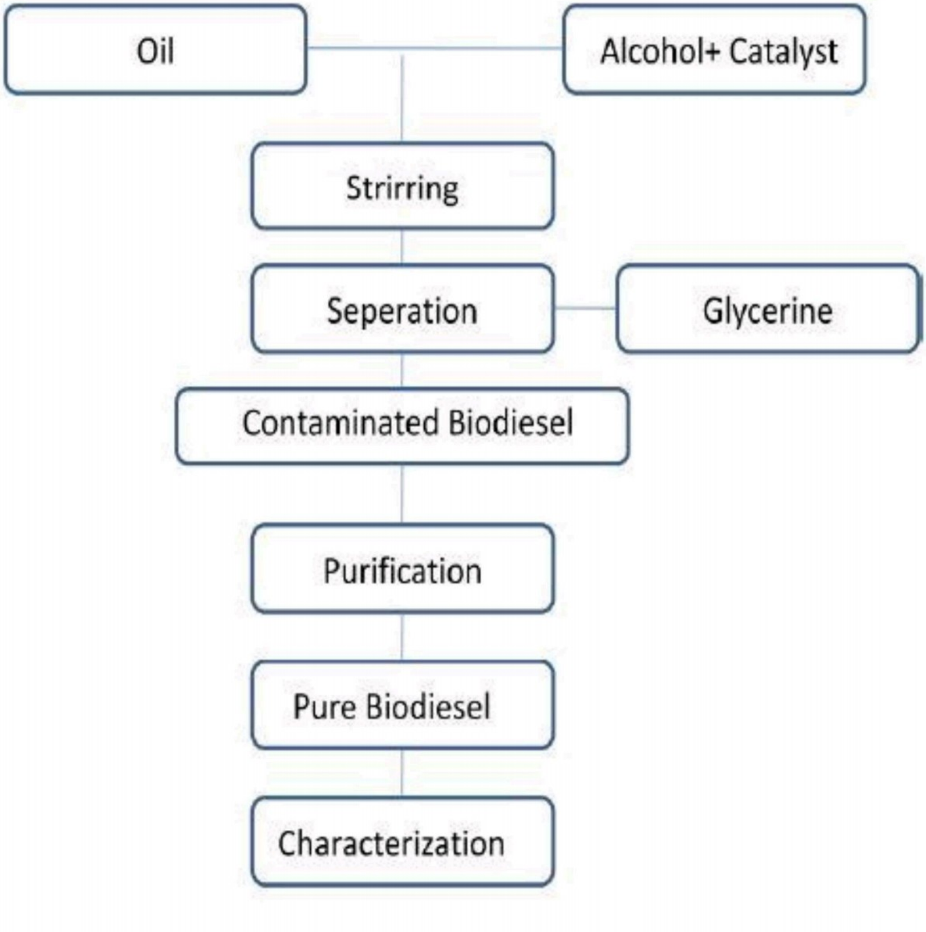


Figure 4.3 Production of Biodiesel

Diesel

Diesel is the middle distillate which is obtained by hydrocracking of gasoil and hydrotreating of distillate obtained from atmospheric and vacuum distillation processes. The crucial specifications of diesel fuels are Sulphur, cetane number and pour/cloud point. Cetane number tells us about the burning quality of the fuel in an engine.

4.2 Graphs and Methods

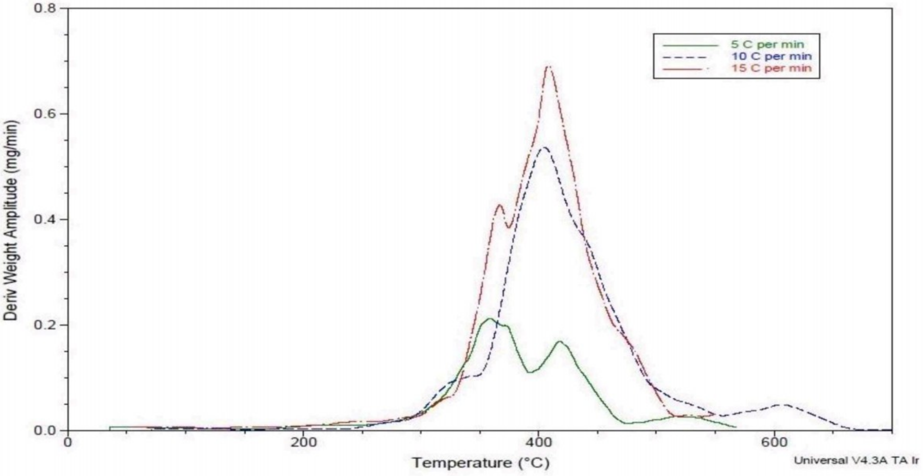


Figure 4.4 (a) DTG Curve for Canola Oil (Pure) at different Heating Rate (5 °C/min, 10 °C/min, 15 °C/min)

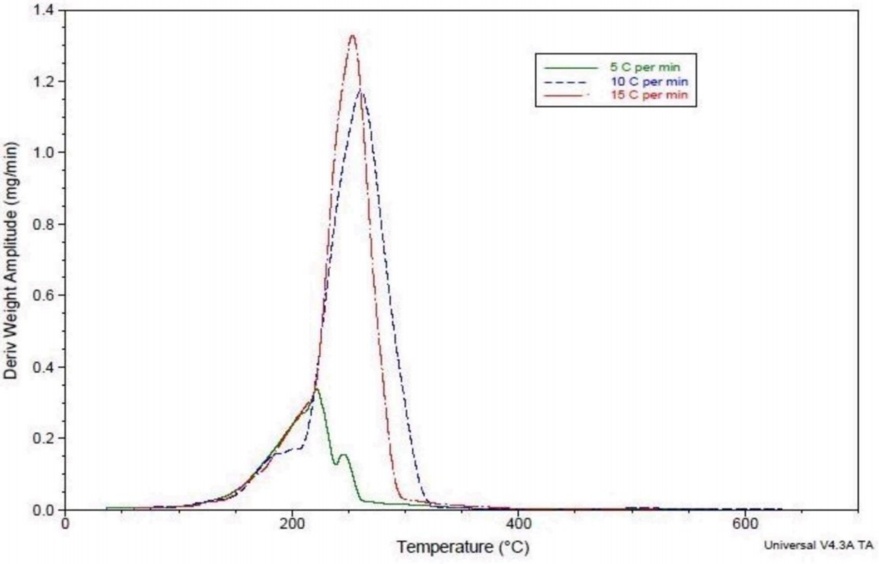


Figure 4.4(b) DTG Curve for Bio -Diesel at different Heating Rate (5 °C/min, 10 °C/min, 15 °C/min)

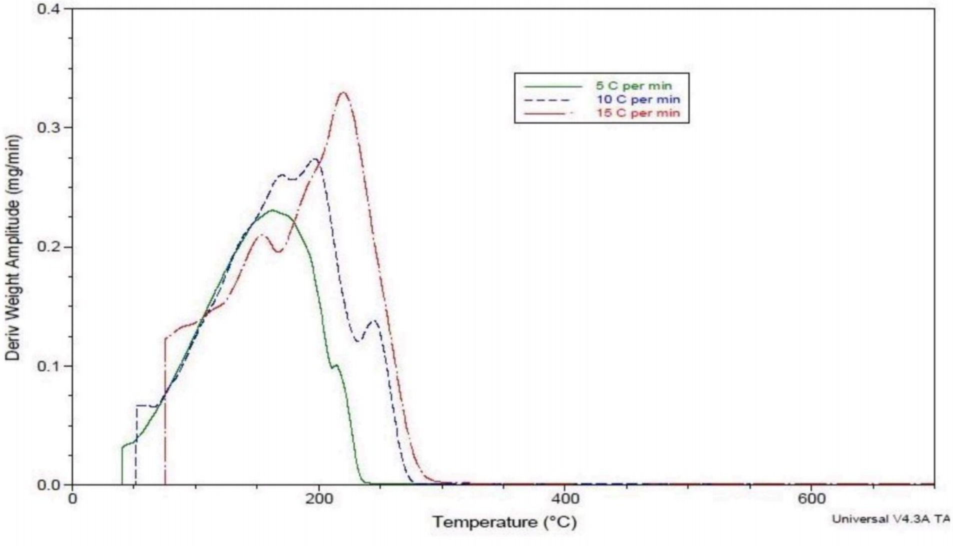


Figure 4.4(c) DTG Curve for Diesel at different Heating Rate (5 °C/min, 10 °C/min, 15 °C/min)

Now as we have obtained these DTG graphs from Thermal Gravimetric Analysis. We will apply Kissinger's model for evaluation of activation energy so that we can comment on the ignitability of the fuels, diesel, canola oil and its biodiesel and how does the activation energy differ from the actual activation energy of the individual component.

As discussed in above chapter, we must find the peak temperature (Tm) and put it into expression and model for further calculation. Now the calculations for this are given below.

Table 4.1 Canola Oil Calculations

Temp(°C)	Tm(K)	Heating Rate(°C/min)	Y-axis ln(beta/tm^2)	X-axis 1/Tm(K)	Slope (-Ea./R)	Activation Energy
Peak 1						
358.4	631.55	5	-11.2869163	0.0015834		Ea1
344.4	617.55	10	-10.548935	0.0016193	-2987.1882	-24.835483
366.8	639.95	15	-10.2147299	0.0015626		
Peak 2						
371.467	644.617	5	-11.3278748	0.0015513		
404.133	677.283	10	-10.7335933	0.0014765	-10381.177	-86.3091059
407.467	680.617	15	-10.3379493	0.0014693		
Peak 3						
528.267	801.417	5	-11.7633249	0.0012478		
607.6	880.75	10	-11.2589625	0.0011354	-4095.9465	-34.0536993
671.6	944.75	15	-10.9937905	0.0010585		

Total activation energy (Ea.) = (24.835483+86.30911059+34.0536993) kJ/mol

= 145.19829289 kJ/mol

Table 4.2 Diesel Oil Calculations

Temp(°C)	Tm(K)	Heating Rate (°C/min)	Y-axis ln(beta/tm^2)	X-axis 1/Tm(K)	Slope (-Ea./R)	Activation Energy
Peak 1						
161.68	434.83	5	-10.5404724	0.0022997		
197.507	470.657	10	-10.0056741	0.0021247	-3081.4533	-25.6192031
220.472	493.622	15	-9.69548988	0.0020258		
Peak 2						
214.961	488.111	5	-10.7716478	0.0020487		
246.194	519.344	10	-10.2025479	0.0019255	-3580.863	-29.7712954
279.265	552.415	15	-9.92054895	0.0018102		

Total activation energy (Ea.) = (25.6192031+29.7712954) kJ/mol

= 55.3904985 kJ/mol

Table 4.3 Biodiesel Oil Calculations

Temp(°C)	Tm(K)	Heating Rate(°C/min)	Y-axis ln(beta/tm^2)	X-axis 1/Tm(K)	Slope (-Ea./R)	Activation Energy
Peak 1						
244	517.15	5	-10.887228	0.0019337		
270	543.15	10	-10.292186	0.0018411	-6781.4161	-56.3806938
284	557.15	15	-9.93761881	0.0017948		
Peak 2						
221	494.15	5	-10.7962403	0.0020237		
260	533.15	10	-10.2550205	0.0018756	-4982.9366	-41.428135
252	525.15	15	-9.81931767	0.0019042		

Total activation energy (Ea.) = (56.3806938+41.428135) kJ/mol

= 97.8088288 kJ/mol

Similarly, all the above things we have done for canola oil we will be applying on this fuel, first we have obtained the DTG Curve from TGA experiment and then using that we have applied model on feedstock oil (peanut oil here) and its biodiesel and based on the results obtained as activation energy we will comment on ignitability. Given below the graph of DTG curve for peanut oil and its biodiesel at different heating rates.

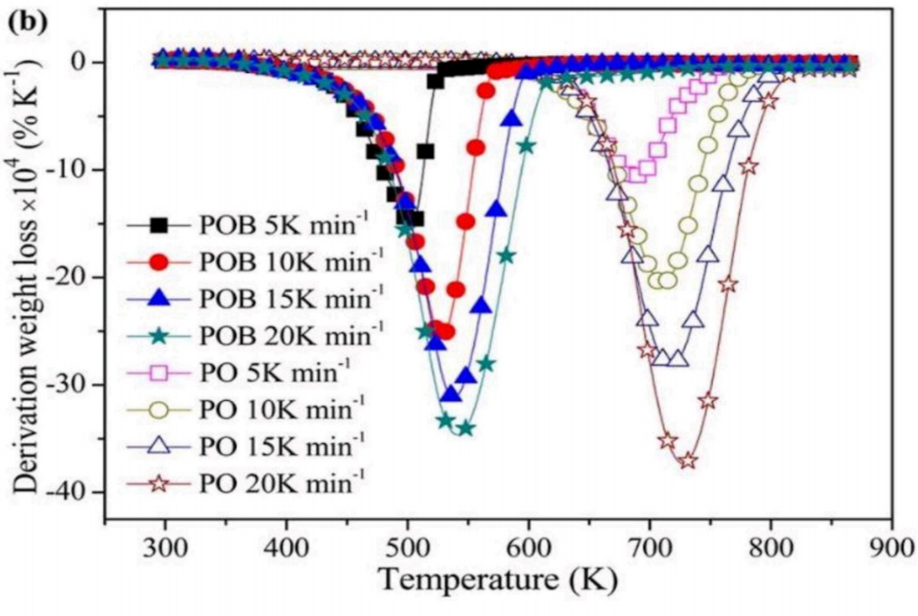


Figure 4.5 DTG curve for Peanut Oil (PO) And its biodiesel (POB) at different Heating Rates(°C/min)

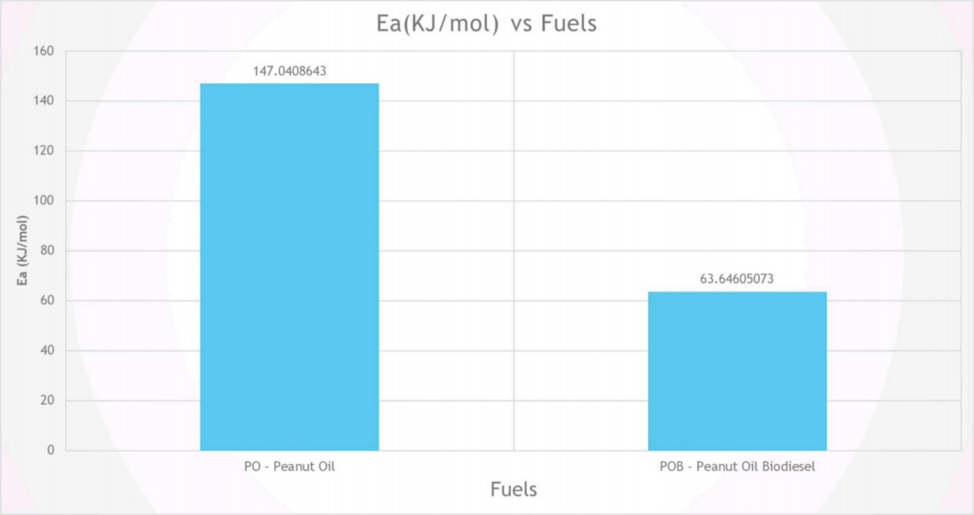


Figure 4.6 Comparison of activation energy of PO and POB

4.3 Results

Now we have the activation energy these fuels (CO, COB, Diesel), we can clearly see that canola oil is having the highest activation energy blending it with diesel in the presence of catalyst through the process of transesterification we have obtained a biofuel which have an activation energy which lies between the activation energies of Diesel and Canola Oil.

Concluding, we can comment on the ignitability order as:

Canola Oil< Canola Oil Biodiesel<Diesel

Also, for PO and POB we can see that activation energy of Peanut Oil is far more than its biodiesel. Hence, we can comment on the order of ignitability as:

Peanut Oil<Peanut Oil Biodiesel<Biodiesel

CHAPTER 5

Bitumen Coal – Pine Sawdust Blend

5.1 Material and Combination
5.2 Graphs and Methods
5.3 Results

Co combustion of coal and Pinus sawdust waste is a cost-effective and long-term solution for enhancing biomass's contribution to energy generation. This technique may potentially be used to minimize greenhouse gas emissions from existing coal-fired power stations. Thermogravimetric analysis was used to explore the thermal synergistic effects of co combusting Hwange bituminous coal (HC) with Pinus sawdust (PS). The experimental setup included fuel blending mass ratios of 100HC, 90HC10PS (90% Hwange Bituminous Coal with 10% Pinus Sawdust), 80HC20PS, 70HC30PS, and 100PS in an oxidative environment at three different heating speeds of 5, 12.5, and 20 C/min. At various blending ratios, zero to negative synergy was seen for the mass loss curves (TG).

5.1 Material and Combinations

Large timber mills use just 10% of the sawdust in their process boilers and lumber drying kilns, allowing the rest to be stored. These sawdust waste stockpiles eventually decompose or, in most cases, succumb to spontaneous combustion, both of which are regarded extreme kinds of pollution or threats to the environment.

Low-grade bituminous coal is the most common type of thermal coal utilized in power plants around the region. Unfortunately, clean coal technologies were not used to assist minimize the region's carbon impact due to coal mining. Carbon dioxide, nitrogen oxides, Sulphur oxides, and particulate matter are all known to be produced in substantial quantities by convectional coal burning on its own. As a result, co-combustion of coal and biomass waste offers a combined method to reducing emissions and improving boiler combustion efficiency. Most co-combustion applications are in industrialized nations.

Here we will be using 90HC10PS (90% Hwange Bituminous Coal with 10% Pinus Sawdust)

5.2 Graphs and Methods

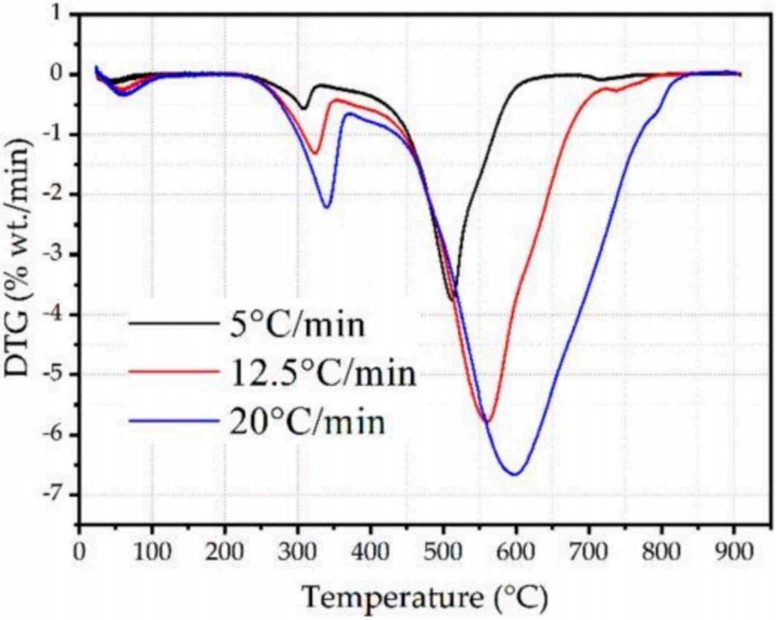


Figure 5.1 DTG Graph for 90HC10PS for different heating rates (5 °C/min, 12.5 °C/min, 20 °C/min)

Now as we have obtained these DTG graphs from Thermal Gravimetric Analysis. We will apply Kissinger's model for evaluation of activation energy so that we can comment on the ignitability of the fuels, diesel, canola oil and its biodiesel and how does the activation energy differ from the actual activation energy of the individual component.

As discussed in above chapter, we must find the peak temperature (Tm) and put it into expression and model for further calculation. Now the calculations done in above method is tabulated below.

Table 5.1 90HC10PS Calculations

Temp(°C/min)	Tm(K)	1/Tm	Heating Rate (β)	Y-Axis ln(β/tm^2)	Slope (-Ea./R)	Activation Energy
PEAK 1						
597.84483	870.99483	0.0011481	20	-10.5435398		
560.99138	834.14138	0.0011988	12.5	-10.92707717	-9764.502	81.1821
513.90086	787.05086	0.0012706	5	-11.72714784		
PEAK 2						
339.87069	613.02069	0.0016313	20	-9.8410651		
323.49138	596.64138	0.001676	12.5	-10.25690381	-14838.427	123.367
309.15948	582.30948	0.0017173	5	-11.12456621		

5.3 Results

By applying Kissinger’s model, we will get activation energy of 90HC10PS to be 204.549 kJ/mol.

Wood, Heat Treated Wood, Impregnated Wood, and Impregnated Wood with Heat Treatment

6.1 Materials and Combinations
6.2 Graphs and Methods
6.3 Results

Wood based biomass is essential for energy production. The production and consumption of modified wood are increasing mainly due to the shortage of high-quality wood from natural forests and the insufficient wood properties of plantation forests. Pyrolysis is used to decompose organic biomass fuels to produce energy-rich oil and gas. It is the process in which biomass is heated in the absence or limited supply of oxygen.

6.1 Materials and Combinations

We used poplar timber as a sample. 34 samples were taken with a length of 1300mm and no observable defect. Moisture content was dropped to 15% using kiln-drying. Then each sample was cut into three sections: Sections A and B with the dimensions of 20 mm× 100 mm × 320mm and C with the dimensions of 640mm mm × 20 mm × 100 (longitudinal, radial, and tangential). Section A was used as the untreated (controlled), whereas Heat Treated was given to Section B as shown in Fig 8. Section C was impregnated with resin. A urea-formaldehyde-e (UF) resin of low molecular weigh

t, modified with melamine is used for impregnation. Table 8 presents the details of the impregnated UF resin. The impregnation of wood with resin is done at a vacuum pressure of 3.0 MPa for 1h on the entire Section C and then dried until the MC was 16%. After impregnation, the increase in dry weight of samples varied from 16.81% to 18.11%.

Technical specifications	Properties
Appearance	Colorless transparent liquid
pH value	8.57
Viscosity (mPa*s(23±0.5˚C))	1.5
Solid content (%)	19.56 (the solid content of original solution is about 50%)
Storage life (d)	≥40

Table 6.1 Details of UF resin used for impregnation

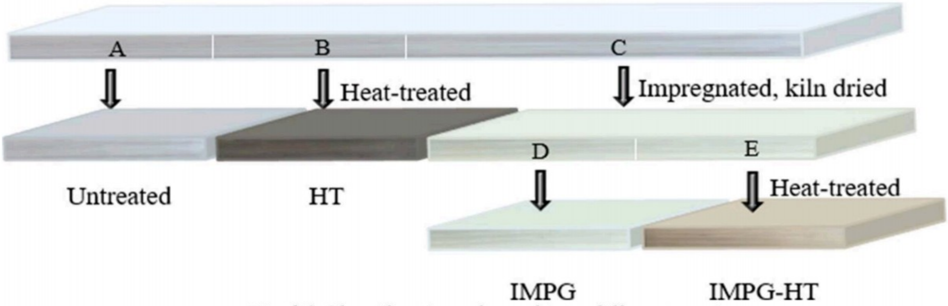


Fig 6.1 Classification of wood into different section

In Fig 1, Section C, impregnated with resin, was divided into two sections: D and E. D was marked as IMPG samples, and E was heat-treated to produce IMPG-HT samples. Section B was labelled as HT samples. HT temperature was 180˚C and duration was 3h.

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6.2 Graphs and Methods

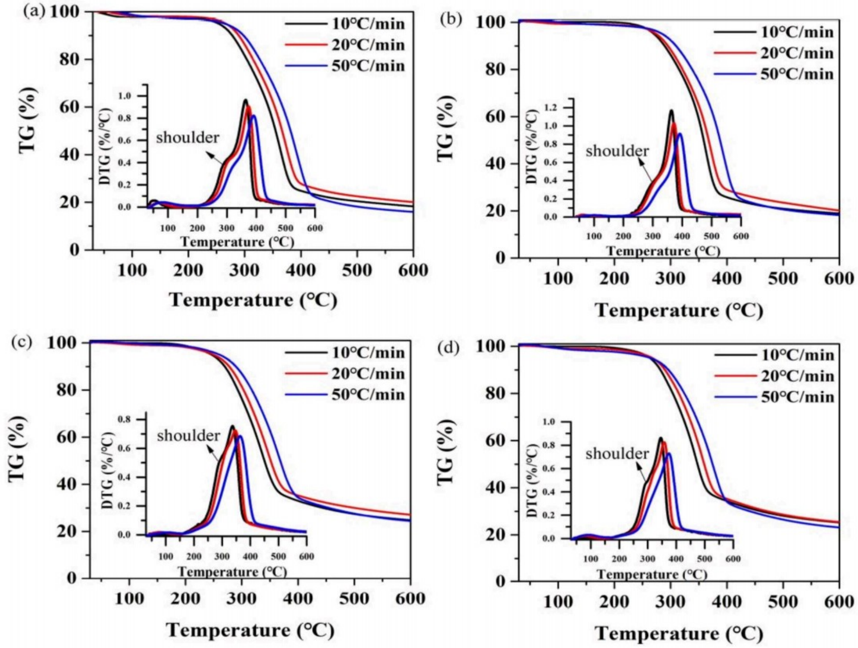

Fig 6.2 TG-DTG curves at different heating rates. (a) TG-DTG curves for untreated samples at heating rates of 10◦C/min, 20◦C/min, and 50◦C/min; (b) TG-DTG curves for HT samples at heating rates of 10◦C/min, 20◦C/min, and 50◦C/min; (c) TG-DTG curves for IMPG samples at heating rates of 10◦C/min, 20◦C/min, and 50◦C/min; (d) TG-DTG curves for IMPG-HT samples at heating rates of 10◦C/min, 20◦C/min, and 50◦C/min.

For all the above graphs obtained from TGA we will apply Kissinger’s model to calculate the final activation energy as discussed in chapter 2.

6.3 Results

We observe that the activation energy of wood is around 200 KJ/mol. The Heat-treated wood has lower activation energy whereas the impregnated wood has slightly higher activation energy. The sample with impregnation and heat treatment has activation energy between the maximum and minimum values.

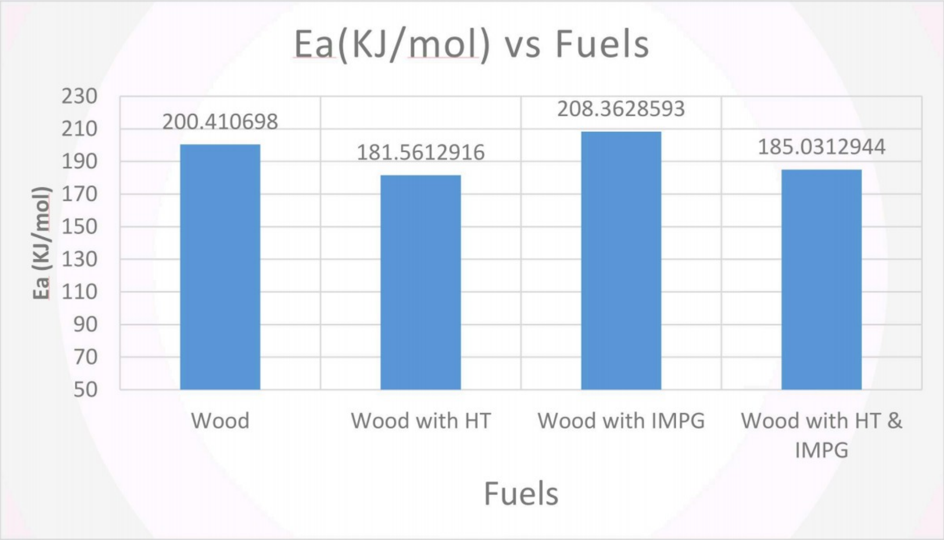

Figure 6.3 Activation Energy of Wood with different types of treatments.

So, the HT promotes pyrolysis, whereas IMPG inhibits pyrolysis.

CHAPTER 7

Conclusions and Discussions
7.1 Activation Energy Representation
7.2 Conclusion for individual fuel

7.1 Activation Energy Representation

SR.	Fuel Name	Activation Energy [Ea. (kJ/mol)]	Method Used
1	DS0 —Cereal Straw without additive	418.0631	Kissinger
2	DS4 - Cereal Straw with halloysite additive	438.6428271	Kissinger
3	PO - Peanut Oil	147.0408643	Kissinger
4	POB - Peanut Oil Biodiesel	63.64605073	Kissinger
5	Wood	200.410698	Kissinger
6	Wood with HT	181.5612916	Kissinger
7	Wood with IMPG	208.3628593	Kissinger
8	Wood with HT & IMPG	185.0312944	Kissinger
9	90% Bituminous coal (HC) with 10% Pine Sawdust (PS)	204.549	Kissinger
10	Canola Oil	145.3491401	Kissinger
11.	Canola Oil Biodiesel	105.1266395	Kissinger
12	Diesel	56.11851403	Kissinger

Table 7.1 Activation Energy of all fuels evaluated using Kissinger Method

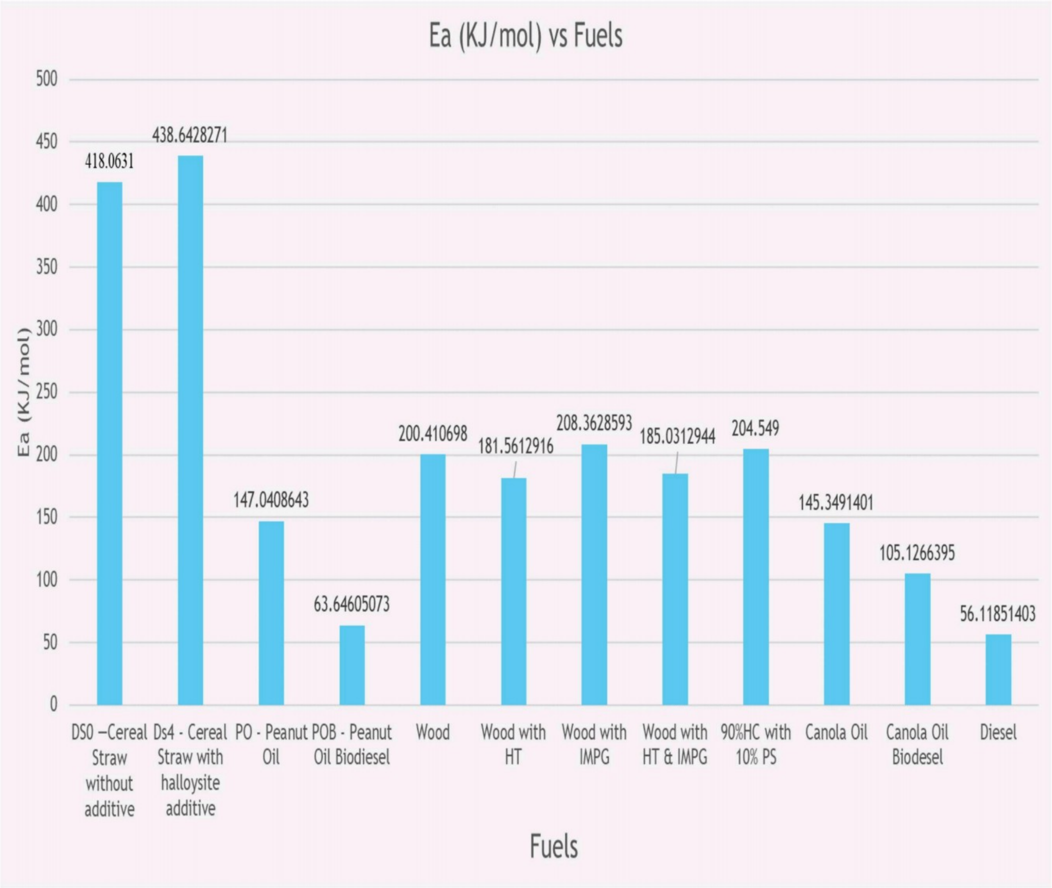

Figure 7.1 Comparison of activation energy of all fuels

7.2 Conclusion for individual fuel

Cereal Straw

The activation energy of the sample with halloysite additive is slightly more because extra energy is consumed in the decay of halloysite additive.

Peanut Oil, Canola Oil, Biodiesel, and Diesel

Now one trend that we can see is that after transesterification, the activation energy of fuel decreases. The activation energy of biodiesels is less than its oils.

If we study the transesterification, we see triglycerides are converted into esters which are our biodiesel. For instance, if we consider fatty acid methyl ester as our product then methyl esters are highly flammable as compared to triglycerides. In general, the esters have 12-15 units higher cetane numbers than their unesterified counterparts.

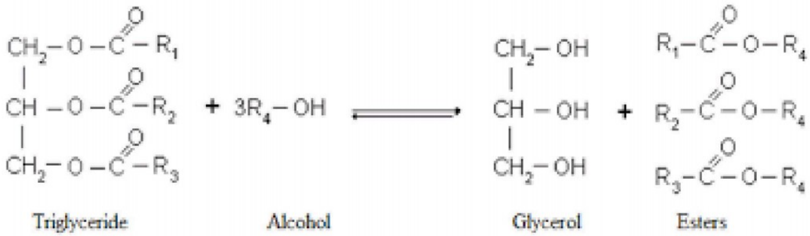

Figure 7.2 General Equation of transesterification

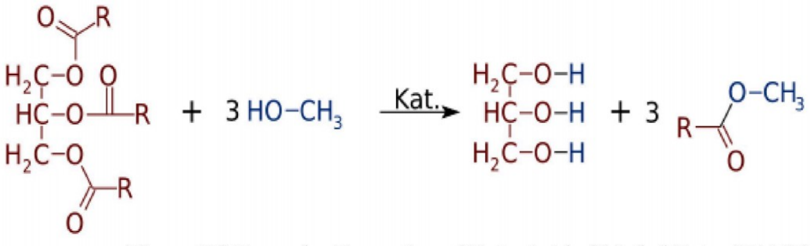

Figure 7.3 Example: Formation of Fatty Acid of Methyl Ester (FAME)

Cetane number is a parameter used to study the ignitibility of diesel fuels. A high cetane number means a low ignition delay. So, the speed of self-ignition of fuel is high when injected with hot air through the fuel injector.

The Heat of Combustion of FAME per unit weight is also slightly higher than TG (Triglyceride) with the same fatty acid composition.

Thus, higher Cetane number and Heat of Combustion represent improved fuel quality.

Wood

For Wood, we see that Heat Treatment decreases its Activation energy, but Impregnation does the opposite. Heat treatment results in the partial decomposition of hemicellulose as well as resin which promotes pyrolysis. The higher activation energy of IMPG is due to the assistance in crosslinking of wood components by resin, thus inhibiting pyrolysis.

Hwange Bituminous Coal and Pinus Sawdust

The change in activation energy of the final fuel occurs due to the synergic effect which inhibits one's ignitability and enhances other ones hence final activation energy comes between the activation energy of Bitumen Coal and Pine Sawdust.

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[6] Combustion Characterisation of Bituminous Coal and Pinus Sawdust Blends by Use of Thermo-Gravimetric Analysis by Garikai T. Marangwanda,Daniel M. Madyira , Patrick G. Ndungu and Chido H. Chihobo

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