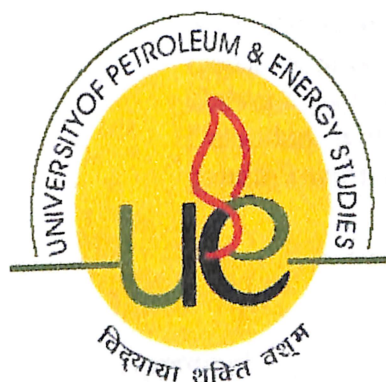


SOLVOLYSIS KINETIC STUDIES OF PINE NEEDLES AND PINE CONES

By
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College of Engineering
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Dehradun
April, 2011

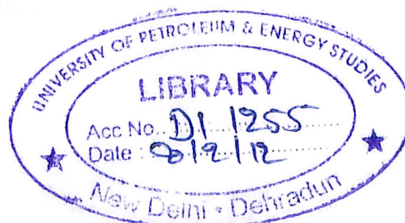
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SOLVOLYSIS KINETIC STUDIES OF PINE NEEDLES AND PINE CONES

A thesis submitted in partial fulfilment of the requirements for the Degree of

Master of Technology

(Process Design Engineering)

By
Santhoshini Priya . T

Under the guidance of

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Approved

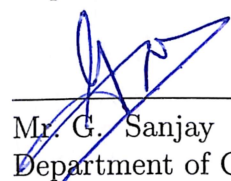
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College of Engineering
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Dehradun
April, 2011

**THE UNIVERSITY OF PETROLEUM AND
ENERGY STUDIES
FACULTY OF ENGINEERING**

The undersigned certify that they have read, and recommend to the Faculty of Engineering for acceptance, a thesis entitled "CHARACTERIZATION AND SOLVOLYSIS KINETIC STUDIES ON PINE NEEDLES AND PINE CONES IN ETHYLENE GLYCOL " submitted by Santhoshini Priya. T in partial fulfillment of the requirements for the degree of M. TECH IN PROCESS DESIGN ENGINEERING.

Head of the Department
Department of Chemical Engineering



Mr. G. Sanjay Kumar
Department of Chemical Engineering

Date

Abstract

This project involves characterization of biomass available in Uttarakhand through degradation kinetics study. Experiments were conducted to liquefy the biomass via solvolysis. The wood is first dissolved in an organic solvent acidified with small amount of H_2SO_4 in mild temperature and pressure condition. H_2SO_4 when present in an amount not higher than 1% with respect to dry wood gave best experimental condition. A mixture of ethylene glycol is a good solvent media and can be recycled in batch tests. It is seen that conversion of biomass increases with increase in reaction temperature and time. Typical kinetic parameters along with percent reacted biomass is determined by using kinetic model. The kinetic studies show that solvolysis with Sulphuric acid at 200-250°C follows a first order reaction. Activation energy is determined from Arrhenius plot.

Acknowledgement

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Chapter 1

Introduction

1.1 Biomass Energy

With the diminishing petroleum reserves and the growing concerns about global climate change, woody biomass is drawing increasing attention as a renewable energy sources due to the advantages of its renewal and abundant(Hongato). Moreover, using it as fuel does not contribute to a net rise in the level of CO₂ in the atmosphere and is much more environmentally friendly. Renewable energy is growing important in responding to concerns over the environment pollution and the shortage of energy supplies. Biomass is viewed as one of the most important potential and the only carbon-containing renewable energy resources. The term biomass can generally be defined as all the biologically produced matter, mainly in form of abundant agricultural and forestry wastes.

1.2 Importance of Biomass

Biomass has always been a major source of energy for mankind from ancient times. Presently, it contributes around 10-14% of the world's energy supply. Biomass can be converted into three main types of products:

1. electrical/heat energy,
2. fuel for transport sector and

3. feedstock for chemicals

Biomass usage as a source of energy is of interest due to the following envisaged benefits:

- Biomass is a renewable, potentially sustainable and relatively environmentally friendly source of energy
- A huge array of diverse materials, frequently stereo chemically defined, are available from the biomass giving the user many new structural features to exploit.
- Increased use of biomass would extend the lifetime of diminishing crude oil supplies.
- Biomass fuels have negligible sulfur content and, therefore, do not contribute to sulfur dioxide emissions that cause acid rain.
- The combustion of biomass produces less ash than coal combustion and the ash produced can be used as a soil additive on farms, etc.
- The combustion of agricultural and forestry residues and Municipal Solid Wastes (MSW) for energy production is an effective use of waste products that reduces the significant problem of waste disposal, particularly in municipal areas.
- Biomass is a domestic resource which is not subject to world price fluctuations or the supply uncertainties as of imported fuels.

- Biomass provides a clean, renewable energy source that could improve our environment, economy and energy securities.
- Biomass usage could be a way to prevent more carbon dioxide production in the atmosphere as it does not increase the atmospheric carbon dioxide level.

1.3 Biomass Components

The importance of particular type of biomass depends on the chemical and physical properties of the large molecules from which it is made. The chemical structure and major organic components in biomass are important in the development of processes for producing derived fuel and chemicals. Biomass contains varying amounts of cellulose, hemicelluloses, lignin and a small amount of extractive. Cellulose is a glucose polymer containing linear chains of (1,4)-D-glucopyranose units, in which the units are linked 1-4 in the alpha configuration, with an average molecular weight of around 100,000. Alpha cellulose is a polysaccharide having the general formulae ($C_6H_{10}O_5$). Hemicelluloses are complex polysaccharides that exist in association with cellulose in the cell wall. It is a mixture of polysaccharides, composed almost entirely of sugars such as glucose, mannose, xylose and arabinose and methyglucuronic and galaturonic acids, with an average molecular weight of 30, 000. Lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of the certain biomass, especially woody species, and are often adjacent to cellulose fibers to form a lignocellulosic complex. In biomass, cellulose is generally the largest fraction, about 40-50% by weight and hemicellulose about 20-40%. McKendry [8] .

1.4 Thermochemical conversion of biomass

Biochemical (such as methane and alcoholic fermentation) and thermal-chemical conversion technologies and processes utilize biomass as feedstock for chemicals and bio-fuels. Four processes can be used to produce fuels from biomass: pyrolysis, solvolysis or liquefaction, gasification and biological conversion. Thermochemical ways are much more rapid than the biological way. However, pyrolysis and gasification both require high operating temperatures which, in the case of pyrolysis, can lead to cross-linking reactions between hydrocarbons and aromatics, yielding a tar which is difficult to further decompose. However, less energy is required for the solvolysis or liquefaction reactions which can be carried out at relatively low temperatures. Hence in these methods, solvolysis is considered to be most promising method obtaining low molecular weight liquid, gas fuel and solid residue.

1.5 Objectives

The objectives of this project are,

1. To characterize locally available biomass in Uttarakhand (primarily pine needles/cones/other forest/agri-residue).
2. Study the co-degradation of such locally available biomass and hydrocarbon oils by thermal and/or chemical processes in a batch reactor.

Chapter 2

Literature Review

2.1 Potential of biomass

Biomass contributes to about 14% of the total energy supply worldwide. India, being a tropical country, has tremendous potential for energy generation through biomass and its residues. Biomass energy is normally produced from firewood, agricultural residues such as bagasse, crop stalks, animal dung and wastes generated from agro-based industries. In India, biomass energy is being utilized mainly for domestic, commercial applications. Liquefaction of biomass provides a promising option for production of liquid fuels for industrial applications.

2.2 Development of solvolysis

Ammar *et al* [2] showed that the liquefaction of wood has been studied extensively in order to provide a liquid fuel, which is easily pumpable, in place of the common products from the petroleum industry. The first attempts undertook the direct liquefaction of wood in one step, achieved as in the liquefaction of coal. This method requires a reducing gas, H₂ or CO at high pressure, a catalyst and a carrier solvent. Unfortunately, the attempts to design and develop continuous pilot units for wood liquefaction have been too seldom: most of the researchers have worked only at a laboratory scale. However, the direct liquefaction of wood is not in favour because

of the technical difficulties in controlling a continuous process. Therefore, attention was focused on a two-step process, in which the first step is a flash pyrolysis and the second is an upgrading of the produced tar, either by hydrotreatment or by cracking on zeolites catalysts. An alternative way to achieve the flash pyrolysis could be the solvolysis of wood in an organic or recycled solvent, without drying and milling the wood to the same extent as that required for the flash solvolysis. The ideal solvent is expected to be cheap and easily recyclable. The ability of oxygenated organic compounds to dissolve wood has long been known. The main solvents tested were simple alcohols, ethylene glycol, phenol and phenol derivatives such as creosol and guaiacol.

2.2.1 Biomass Liquefaction via Solvolysis

Yaman *et.al* [10] stated that among thermal liquefaction conversion, pyrolysis and solvolysis are two main research focuses on converting biomass to more useful chemicals and fuels. Thus far, nearly 100 different biomasses, such as nutshell, corn stover, cherry stones, pinewood, sawdust, have been employed pyrolysis conditions. However, the high operating temperature of pyrolysis can lead to cross-linking reaction between hydrocarbons and aromatics resulting in tar which is difficult to further decompose. Solvolysis has many advantages such as,

1. The presence of solvent dilute the concentration of the products preventing the cross linked reactions and reverse reactions
2. Relative low temperature (less energy consumption) in comparison with pyrolysis and gasification.

Among thermal liquefaction conversion methods, solvolysis is the most widely used method due to relatively lower process temperature as compared to pyrolysis process. This can prevent the formation of tar compounds due to the cross-linking between hydrocarbon and aromatics compounds Liu *et.al* [7] . In the solvolysis process, biomass depolymerizes in the presence of organic reagents to form useful chemicals Lin *et.al* [6] .

Hui [4] demonstrated that the solvolysis liquefaction of biomass dissolves biomass in an organic solvent at moderate temperature of 120 to 250 °C. Partial solvolysis of biomass provides valuable chemicals, mainly pure cellulose and phenolic compounds, and complete solvolysis provides fuels. For producing liquid oil from biomass, the alternative way to flash pyrolysis is liquefaction, i.e. the dissolution of biomass in a liquid medium. This liquid medium can be simply water, eventually with added minerals (acids, bases, salts, catalysts). The primary bio-oil must be upgraded to reach the specifications of a classical petroleum fuel related to its heating value and its viscosity. The liquefied biomass has many potential applications, on one hand as a starting material to produce biopolymer, polyurethane, phenolic resins, adhesives.

2.2.2 Effect of solvent and catalyst

Solvent has remarkable effect on the liquefaction reaction Zhengang *et.al* [19] . Some articles have been reported about the solvolysis liquefaction of biomass and the presences of organic solvents are proven effectively to lower the viscosity of heavy oil derived from biomass liquefaction. Demirbas [1] .

Several investigations have been carried out previously on solvolysis of biomass using different solvents. Yan *et al* [16] investigated the effects of temperature, re-

action time, hydrogen pressure, and type of solvent on the liquefaction of sawdust. They found that solvent has promoted destruction of molecular structure of sawdust. Yip *et al* [18] carried out liquefaction of bamboo using various solvents, i.e., phenol, ethylene glycol, and ethylene carbonate. Meanwhile, liquefactions of pinewood in the presence of various solvents (water, acetone, and ethanol) have also been conducted in the temperature range 523 to 723 K by Liu *et al* [7]. Kunaver *et al* [5] investigated the liquefaction of different types of southern European hardwoods and softwoods using glycerol and diethylene glycol. Yamada *et al* [15] reported the liquefaction of cellulose using ethylene glycol in the presence of hydrochloric acid. The products obtained can be used as raw materials of some functional polymers and chemical products.

Yao *et al* [17] investigated various polyols or their combination with other polar solvents as reagent solvents in biomass liquefaction, such as ethylene glycol (EG), polycaprolactone (PCL303), EG/glycerin, EG/1,1,1-tris (hydroxymethyl) propane (TMP), and caprolactone (CPL)/glycerin. The results showed that the liquefaction reaction using EG/glycerin achieved the lowest residue content among all other tested solvents. Aliphatic alcohols, polyols, phenol and phenol derivatives have probably been the most tested organic solvents. Among Organic solvents, ethylene glycol appeared as a very effective solvent medium, almost as effective as phenol. Moreover, owing to the toxicity of phenol, its use on an industrial scale is prohibited. Aliphatic alcohols (from C1 to C7) or polyols have been known for a long time to selectively dissolve the basic components of wood. Tin *et al* [13]

The experiments of solvolysis were performed by Rezzoug *et al* [9] with a mass ratio solvent/wood of 4/1. In order to investigate the effect of this ratio, some

experiments have confirmed that a minimal ratio of 4/l is required to wet adequately the wood floor and achieve a total dissolution of wood. When using a typical solvent such as ethylene glycol, it is obvious, that an addition of a small amount of H_2SO_4 , greatly enhances the dissolution of wood which occurs at a lower temperature than it does with pure ethylene glycol. At the end of reaction, the increase in residual solid can be explained by the formation of coke from the degradation products of wood and the extent of cokefaction in all cases increases with increasing quantities of strong acid (H_2SO_4) added to the organic solvent. For various solvents, the effect of the H_2SO_4 amount was tested in the range 0-3% (on the dry wood basis); nevertheless about 1% H_2SO_4 seems to be the optimal value to achieve a maximal dissolution of wood at moderate temperature.

Rezzoug *et al* [12] further showed that both strong acids, such as sulfuric acid and hydrochloric acid, and weak acid, such as oxalic acid, can be used as catalysts in biomass liquefaction. The resulting liquefied wood using a strong acid catalyst can achieve a lower wood residue content than those using a weak acid catalyst. The addition of a small amount of sulfuric acid greatly enhanced the dissolution of wood, which favored hydrolytic cleavages along the cellulosic chain.

2.2.3 Effect of temperature

William *et al* [14] demonstrated that the solubilization of total mass and lignin increases with increasing temperature. However, the solubilization of cellulose and lignin does not increase significantly with time, despite the fact that much of each component remains in the solid. Shiraishi *et al* [11] reported that liquefaction of ligno-cellulosic biomass can be done in the presence of these organic solvents using

acid catalysts at temperatures of 120 to 180 °C or without catalysts at temperatures of 180 to 250°C.

Chapter 3

Materials and Methods

3.1 Proximate Composition of Biomass

3.1.1 Objective

To determine the moisture, volatile and ash contents in a given biomass sample by proximate analysis.

Requirements

Powdered biomass, analytical balance, electric oven, dessicator , silica crucible, tong, muffle furnace.

3.1.2 Procedure

Determination of Inherent Moisture

1gm of air dried biomass sample is taken in the preweighed silica crucible. It is kept inside the electric oven at 105-110°C for an hour. It is cooled in dessicator and weighed. The difference in weight is reported in percentage as the amount of inherent moisture in biomass.

Volatile Matter

The dried biomass sample after determining moisture content heated in a muffle furnace at about 925°C for exactly 7 min. The biomass sample is taken in a crucible

and heated with a lid. It is cooled in the dessicator and weighed. Loss in weight gives the percentage volatile matter.

Ash

The residual biomass in the crucible after the determination of volatile matter in it, is heated without lid in the muffle furnace at about 725°C for half an hour for constant weight. It is cooled in dessicator. The amount of unburnt carbon residue in crucible is ash which can be reported in percentage.

3.1.3 Observations and Calculations

Moisture

Weight of empty crucible = w_1 g

Weight of crucible +sample = w_2 g

Weight of sample = (w_2-w_1) g

Weight of (crucible+ sample) after heating at 110°C = w_3 g

Moisture contents = (w_2-w_3) g

% moisture = $[(w_2-w_3)/(w_2-w_1)] \times 100$

Volatile Matter

Weight of (crucible+sample)after heating at 925°C for 7 min = w_4 g

Volatile matter = (w_3-w_4) g

% of volatile matter = $[(w_3-w_4)/(w_2-w_1)] \times 100$

Ash

Weight of (crucible + ash) = w_5 g

Ash contents = $(w_5 - w_1)$ g

% ash = $[(w_5 - w_1) / (w_2 - w_1)] \times 100$

Sample Calculation :**Determination of moisture content**

Weight of empty crucible = 20

Weight of crucible + sample = 25 g

Weight of sample = $(25 - 20)$ g

Weight of (crucible + sample) after heating at 110°C = 23 g

Moisture contents = $(25 - 23)$ g

% moisture = $[(25 - 23) / (25 - 20)] \times 100$

Determination of volatile matter

Weight of (crucible + sample) after heating at 925°C for 7 min = 22 g

Volatile matter = $(23 - 22)$ g

% of volatile matter = $[(23 - 22) / (25 - 20)] \times 100$

Determination of ash content

Weight of (crucible + ash) = 21 g

Ash contents = $(21 - 20)$ g

$$\% \text{ ash} = [(21-20)/(25-20)] \times 100$$

3.2 Estimation of Calorific Value using Digital Bomb Calorimeter RSB5

3.2.1 Objective

A Bomb-Calorimeter is used to measure the heat created by a sample burned under an oxygen atmosphere in a closed vessel, which is surrounded by water, under controlled conditions.

3.2.2 Procedure

1. About 1g of solid or liquid matter is weighed into a crucible, and placed inside a stainless steel container (the Decomposition vessel) filled with 30 bar (435 PSI) of oxygen.
2. Then the sample is ignited through a cotton thread connected to an ignition wire inside the decomposition vessel and burned (combusted).
3. During the combustion the core temperature in the crucible can go up to 1000°C (1800 °F), and the pressure rises for milliseconds to approximately 200 bar (2900 PSI).
4. All organic matter is burned under these conditions, and oxidized. Even inorganic matter will be oxidized to some extent.

5. The heat created by the combustion process is transferred into the surrounding water.
6. To ensure that the heat created during the combustion does not get out of the system or heat gets into the system from the environment (room temperature changes), another water filled vessel (outer vessel) is used as an isolation.
7. The temperature change in the water is accurately measured. This temperature rise, along with bomb factor is used to calculate the energy given out by the sample burn.
8. After the temperature rise has been measured, the excess pressure in the bomb is released.

3.3 Solvolysis

3.3.1 Objective

To determine the order of reaction, kinetic reaction rate constants, percentage reacted wood for different temperature by solvolysis.

Theory

The speed at which a reaction takes place is of particular importance in chemistry because it provides information about the detailed path over which reactants travel on their way to becoming products (the reaction mechanism). The correct interpretation of rate data depends on knowledge of those factors that can influence the rate and these include

1. The structure of the compound or compounds entering into the reaction,
2. The temperature,
3. The type of solvent in which the reaction is carried out, and
4. for many reactions, the concentrations of the reacting species.

In this experiment, solution of ethylene glycol with concentrated sulphuric acid (1% with respect to biomass) is added to biomass (0.2-0.3mm mesh). Ethylene glycol is more effective solvent medium, almost as effective as phenol. 1% sulphuric acid is found to be an optimal value to achieve a maximal dissolution of wood at moderate temperature.

Requirements

500ml three neck flask(borosilicate), thermometer, laboratory stirrer, water circulating pump, heating mantle, condenser, pipette, sample vial, spatula, acid gloves, ordinary filter paper, oven, ethylene glycol, sulphuric acid, acetone, distilled water, funnel, beaker.

3.3.2 Procedure

1. Grind biomass using crusher and make it to 0.2-0.3mm mesh size using sievers.
2. Take 1:4 ratio of biomass(pine needle/pine cone): solvent(ethylene glycol).
3. Take 1% of sulphuric acid with respect to weight of biomass.
4. Put biomass, ethylene glycol, sulphuric acid in to three neck flask equipped with laboratory stirrer and thermometer.

5. The reaction temperature is 200-250°C for various reaction time.
6. After reaction reaches set time, turn off stirrer and mantle. Cool the flask to room temperature.
7. Content in the flask is filtered with ordinary filter paper.
8. Unreacted residue is washed well with acetone, dried in an oven at 110°C and weighed.
9. The yield of solvolysis X (conversion) is thus defined by
$$X = \frac{\text{Mass of acetone soluble material}}{\text{Mass of initial dry wood}} \text{ (g)}$$
10. The acidity of solvolysis oil is determined by the dilution of 1ml solvolysis oil in 50ml of distilled water.
11. Plot graph for reaction time and unreacted residue content.
12. Determine order of reaction from the graph.
13. Kinetic values are found for different reaction temperature and time.
14. Plot another graph between different temperature and Kinetic Value and determine activation energy from the plot.

Chapter 4

Results and Discussions

4.1 Proximate composition of biomass

S.No	Biomass	Moisture content	Volatile matter	Ash	Fixedcarbon
Units		%	%	%	%
1	Pineneedle	11.67	64.44	4.97	18.92
2	Pine cone	6.74	73.62	3.4	21

Table 4.1: Results of proximate analysis

4.2 Calorific value using Digital bomb calorimeter RSB5

S.No	Biomass	Calorific value
Units		cal/gm
1	Pine needle	3718.15
2	Pine cone	3451.95

Table 4.2: Calorific value using Digital bomb calorimeter

4.3 Solvolysis of pine needles

It is seen from the table 4.3 that the solvolysis of pine needle conversion increases with increase in reaction temperature and time. The temperature is not increased above 250°C in order to stabilize solvolytic oil and to prevent any further cokefaction. The unreacted biomass is increasing with the decrease in temperature below

250°C. The conversion is upto 25 % at 250°C. The decrease in the acidity is due to the consumption of the H⁺ ions due to the hydrolytic scission reactions along the glycosidic chains of cellulosic compounds.

S.No	Time (min)	200°C	225°C	250°C
1	0	5	5	5
2	15	4.93	4.91	4.89
3	30	4.77	4.69	4.53
4	45	4.49	4.35	4.13
5	60	4.27	4.1	3.86

Table 4.3: Solvolysis of pine needles and effect of weight of residue at different temperature

S.No	Time	Acidity
1	15	2.9
2	30	2.5
3	45	2.4
4	60	2.1

Table 4.4: Change in acidity of pine needles at various reaction time

4.4 Solvolysis of pine cones

It is seen from the table 4.5 that the solvolysis of pine cone conversion increases with increase in reaction temperature and time. The temperature is not increased above 250°C in order to stabilize solvolytic oil and to prevent any further cokefaction. The unreacted biomass is increasing with the decrease in temperature below 250°C. The conversion is upto 25 % at 250°C. The decrease in the acidity is due to the consumption of the H⁺ ions due to the hydrolytic scission reactions along the glycosidic chains of cellulosic compounds. However when the reaction time is

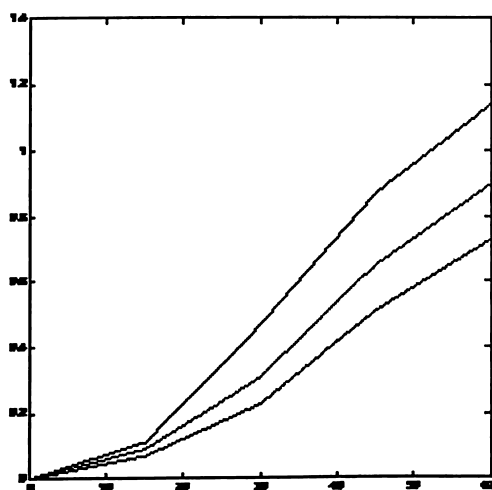


Figure 4.1: Reacted pine needle Versus time at different reaction temperature

prolonged the solid carbonaceous material is generated in the solution, the yield of which is consequently lowered.

S.No	Time (min)	200°C	225°C	250°C	Acidity at 250 ° c
1	0	5	5	5	
2	15	4.94	4.93	4.92	2.6
3	30	4.81	4.75	4.65	2.5
4	45	4.64	4.43	4.22	2.4
5	60	4.28	4.05	3.92	2.3

Table 4.5: Solvolysis of pine cones and effect of weight of residue at different temperature

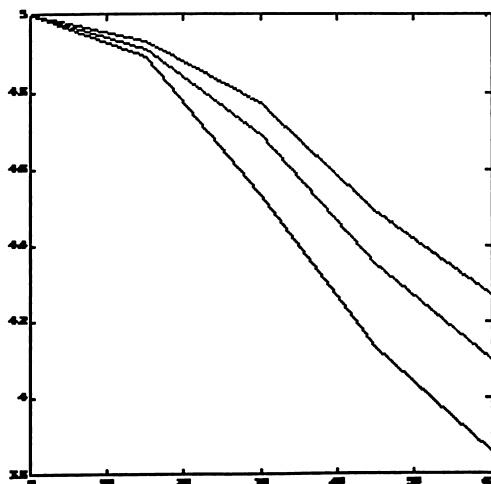


Figure 4.2: Unreacted Pine needle Versus Time at different reaction temperature

4.5 Kinetic values of Pine needles and pine cones at different temperature

Solvolysis of Pine needles and Pine cones have been carried out at three temperatures (namely 200, 225, 250 °c)with ethylene glycol in the presence of sulphuric acid. The wood conversion is measured as a function of time. From figure 4.4, 4.5, the linear variation of $\ln(1-x)$ shows that the reaction is of first order with respect to the unconverted biomass. It is seen that kinetic rate constant of both pine needles and pine cones increases with reaction temperature according to Arrhenius law. The rate constant of a reaction increases with temperature because a greater fraction of reactant molecules has enough energy to pass over the energy barrier.

From the figure 4.4, 4.5, Kinetic values of pine needles and Pine cones for different temperature is found and given in table 4.6 and 4.7 respectively.

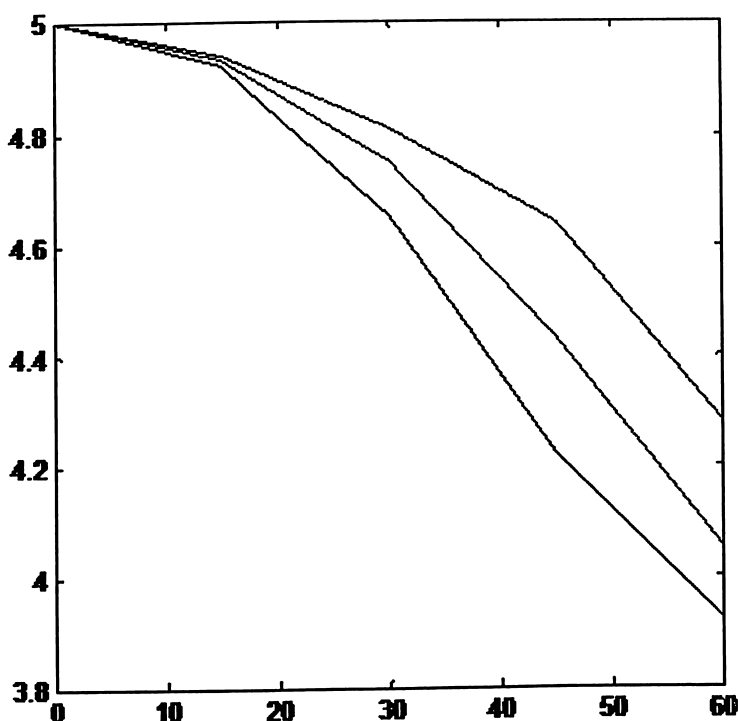


Figure 4.3: Unreacted pine cone Versus Time at different reaction temperature

4.6 Arrhenius plots for Pine needles and Pine cones

The way the rate constant varies with temperature is described by arrhenius equation.

$$K = Ae^{-\frac{E_a}{RT}} \quad (4.1)$$

A plot of $\ln k$ against $1/T$ gives a straight line with a gradient $-E_a/R$ from the table 4.8 . The activation energy, E_a , is the energy barrier reactants must overcome in order to form products. The activation energy is determined for Pine needles and pine cones from the slope of Arrhenius plot in figure 4.6 and 4.7 respectively.

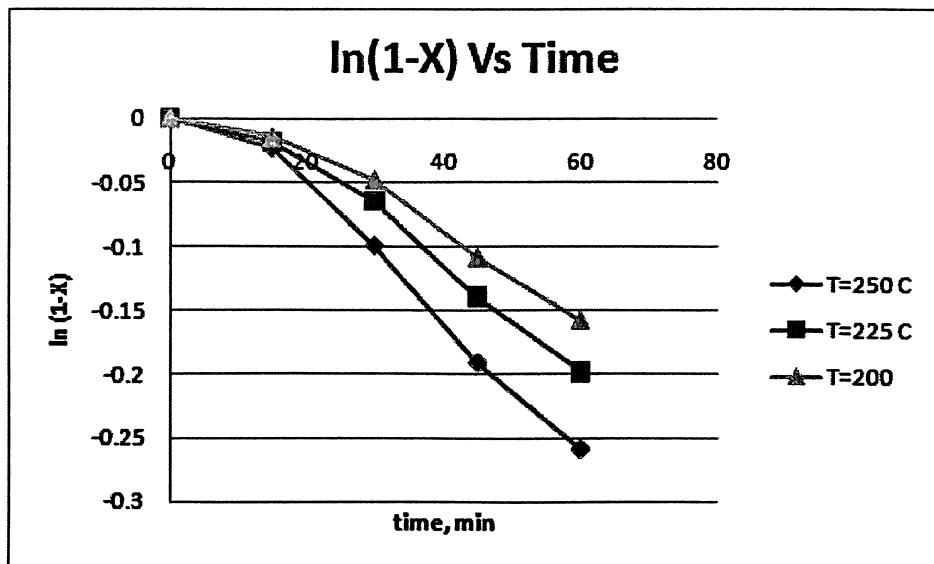


Figure 4.4: $\ln(1-X)$ Vs reaction time for pine needles

S.No	Temperature	Rate constant
1	200	0.00273
2	225	0.00345
3	250	0.00458

Table 4.6: Rate constant for pine needles at different temperature

S.No	Temperature	Rate constant
1	200	0.00249
2	225	0.00352
3	250	0.00426

Table 4.7: Rate constant for pine cones at different temperature

S.No	Biomass	ln K	1/T
1	Pineneedles	-5.386	0.001912
		-5.668	0.002008
		-5.904	0.002114
2	Pine cones	-5.458	0.001912
		-5.649	0.002008
		-5.995	0.002114

Table 4.8: Arrhenius Values for Pine needles and Pine cones

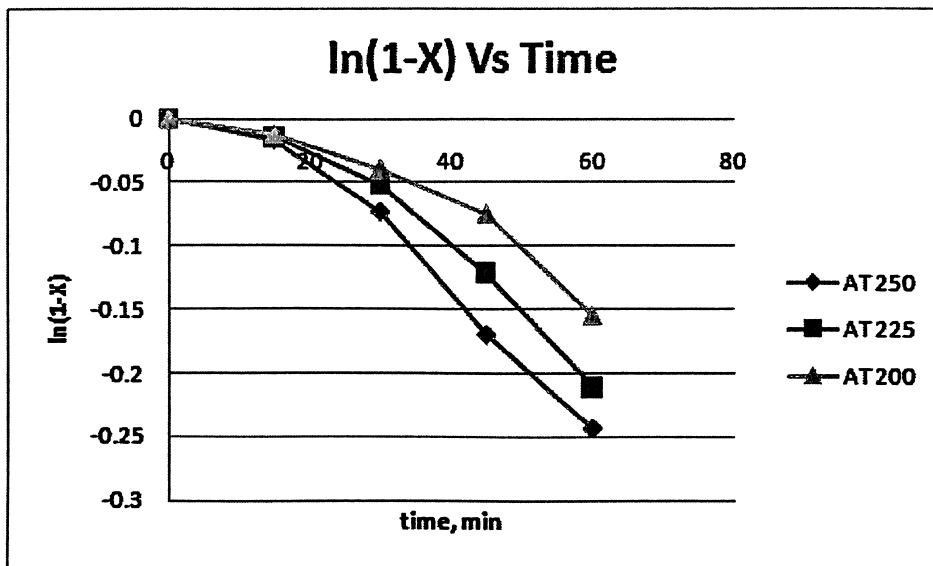


Figure 4.5: $\ln(1-X)$ Vs reaction time for pine cones

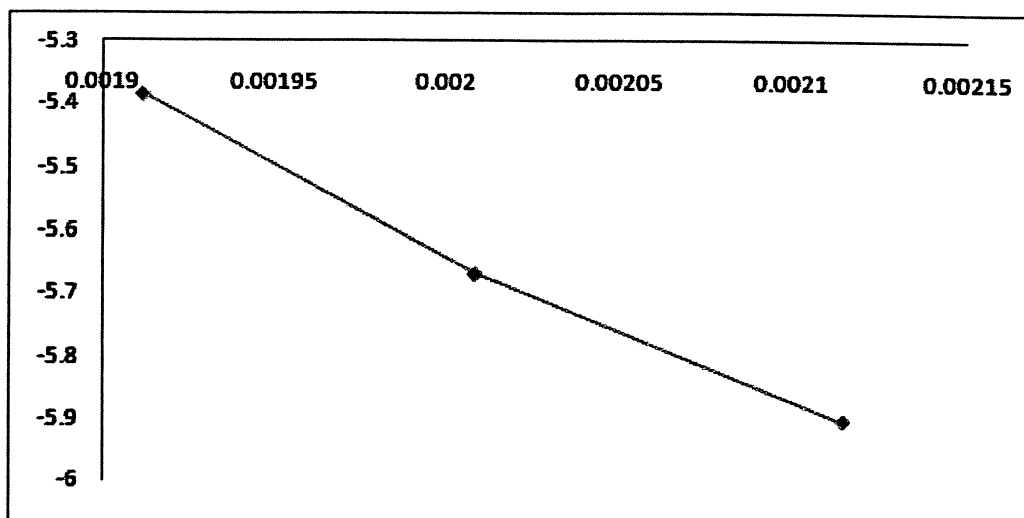


Figure 4.6: Arrhenius plot for Solvolysis of pine needles

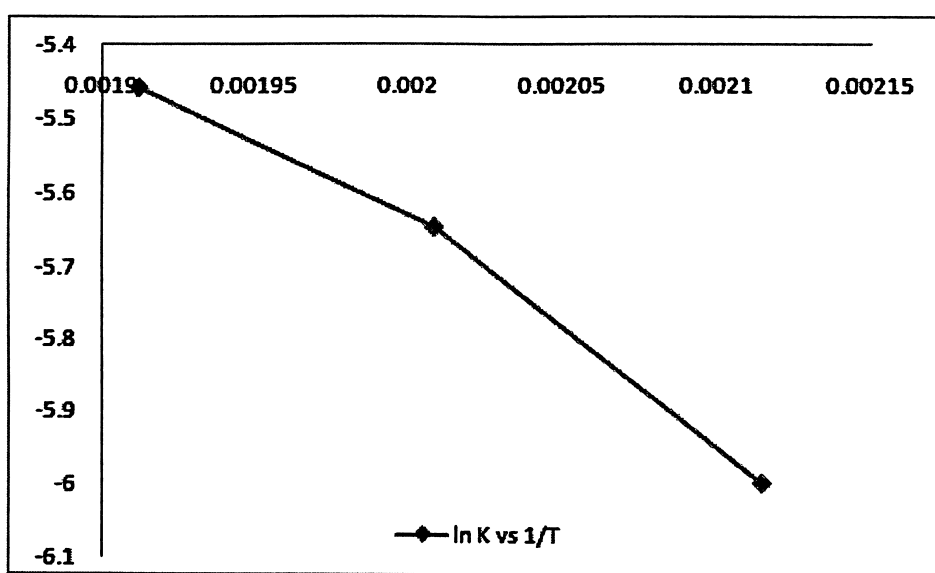


Figure 4.7: Arrhenius plot for solvolysis of pine cones

Chapter 5

Conclusion and Future Scope of Work

The aim of this experimental project is to solvolyze Pine needles and pine cones, to find the conversion behaviour of biomass at different reaction temperature for various reaction time, determine the kinetic rate constants from experimental datas. In this project pine needles and pine cones were solvolyzed in ethylene glycol with 1 % sulphuric acid. Effect of solvolysis on Pine needles and Pine cones were studied for various reaction time and it is seen that both pine needle and pine cones conversion increased with reaction temperature and time. Kinetic rate constants were determined for different reaction temperature and Arrhenius plot to determine the activation energy of Pine needles and Pine cones. It is found at temperature range of 200 - 250 ° c solvolysis of Pine needles and Pine cones obeyed first order reaction. It is seen that the reaction rate constant increases with reaction temperature and time, thus indicating reaction occurs favourably at high temperature due to higher rate constants and higher correlation coefficient values at higher temperature in comparison to other temperature. Activation energy were 21.57 KJ/mol and 22.24 KJ/mol for pine needles and pine cones respectively from Arrhenius plot.

Hydrotreatment can be done in the presence of suitable catalyst to remove oxygen content from the obtained solvolytic oil and to improve the yield. The solvent consumption in solvolysis can be analysed for different reaction time by using HPLC. Products can be analysed for various reaction time by LC/GC. Kinetic rate constants can be determined for analysed products at various reaction time and temperature.

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