MODELING OF PRETREATMENT PROCESS OF LIGNOCELLULOSIC BIOMASS BY DILUTE ACID HYDROLYSIS

THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENT FOR THE DEGREE OF

MASTER OF POWER ENGINEERING

BY

ABHIRUP GHOSH

(UNIVERSITY REGISTRATION NO: 129420 of 2014-15)

(EXAMINATION ROLL NO: M4POW1601)

UNDER THE SUPERVISION OF

PROF. AMITAVA DATTA

FACULTY OF ENGINEERING AND TECHNOLOGY

DEPARTMENT OF POWER ENGINEERING

JADAVPUR UNIVERSITY

Jadavpur University

Faculty of Engineering & Technology

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_____

(THESIS ADVISOR)

COUNTERSIGNED

_____

(HEAD OF THE DEPARTMENT)

_____

(DEAN OF FACULTY OF ENGG. & TECH.)

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I hereby declare that this thesis entitled "*MODELING OF PRETREATMENT PROCESS OF LIGNOCELLULOSIC BIOMASS BY DILUTE ACID HYDROLYSIS*" contains literature survey and original research work by the undersigned candidate, as part of his *Master of Power Engineering* studies. All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

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Name (Block Letters):   ABHIRUP GHOSH

Examination Roll Number: M4POW1601

Registration No: 129420 of 2014-15

Class Roll No: 001411502001

Signature with Date:

Acknowledgement

The author remembers with gratitude the constant guidance, suggestions, encouragement and support forwarded by several respected persons and knows well that it is impossible to express his humility for all those valuable assistances in this finite piece of paper. Following conventions, the author therefore, acknowledges in this page, the assistance rendered by all the concerned persons, as a token of thanks.

The author feels honoured to express his sincerest gratitude to Prof. Amitava Datta, the thesis supervisor for his valuable guidance, friendly encouragement and helping the author to acquire substantial knowledge in preparing the whole process layout, simulation work. Without which this thesis would not have been completed.

The author likes to convey his gratitude to the faculty in M.E. course of Power Engineering department of Jadavpur University for the excellent teaching that has helped a lot to complete the project smoothly.

The author expresses his sincere thanks to all his co-workers Mr. Sunny Kumar Singh, Mr. Mithun Das, Mr. Pritam Kumar Das, Ms. Mayurakshi Mondal , Mr. Atmadeep Bhattacharya, and Ms. Srabanti Ghosh both in the same laboratory and from other laboratories of the department for the valuable time they have spared giving ideas and suggestions wherever and whenever necessary.

Last but not the least the author also expresses his heartiest gratitude to God, parents and friends who have always been a constant inspiration source in each and every work that finally contributed to the successful completion of this work.

Abhirup Ghosh

ABSTRACT

Biomass is one of the most important renewable energy resource which can reduce the dependence on fossil fuels and emission of carbon dioxide. Ethanol converted from celluloses and hemicelluloses in lignocellulosic biomass by biochemical technology has great potential to replace gasoline for transportation fuels. Hemicelluloses contains abundant fermentable five carbon sugars, which can be released by thermal/chemical pre-treatment processes. There are various types of pre-treatment processes. But among them dilute acid pre-treatment is very much efficient and can easily hydrolyse hemicelluloses to monomeric xylose and make the cellulose more sensitive to enzymatic digestion. In this study, a model is developed for hydrolysis of hemicellulose to its xylooligomers and finally xylose by first order reaction. This model also represents oligomers as a single compound and effect of variation of acid and temperature on oligomers have been included in this study. The model is used to find out the production of xylose from three different feedstocks with dilute sulfuric acid (0.5, 1 and 2 %v/v) at relatively high temperatures (140, 150, and 160 ℃) in a reactor. A comparison of optimum production of xylose from these three biomass has been made in this study.

Nomenclature

C_d = Concentration of degradation product

C_X = Concentration of xylose

C_2 = Concentration of xylobiose

C_3 = Concentration of xylotriose

C_4 = Concentration of xylotetrose

C_5 = Concentration of xylopentose

C_W = Concentration of water

K_2 = xylobiose degradation constant (min^{-1})

K_3 = xylotriose degradation constant (min^{-1})

K_4 = xylotetrose degradation constant (min^{-1})

K_5 = xylopentose degradation constant (min^{-1})

K_d = xylose degradation constant (min^{-1})

K_H = Hemicellulose degradation constant (min^{-1})

α_4 = Probability of xylotetrose breakage at the middle (%)

α_5 = Probability of xylopentose breakage at the middle (%)

D = Diffusion coefficient for water and other xylooligomers $(m^2 s^{-1})$

C_a = Actual acid concentration (wt%) of dilute acid solution

E_a = Activation energy in (kJ/mol)

R= Gas constant (kJ/mol-K)

T = Temperature (K)

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1

INTRODUCTION

Over the past one hundred years, energy demand is increasing significantly because of the industrial revolution and population growth. The present energy consumption is mainly dependent upon the fossil fuels like oil, coal, and natural gas etc. Around the middle of the twentieth century, people started to notice that fossil fuels cannot be considered as the main source of energy due to its finite reserve. So we need to look after the energy scenario to fulfil this increasing energy demand.

1.1 Energy Scenario

Energy scenario provides a framework for exploring future energy prospective including various combinations of technology options and their implications. Energy scenario illustrates how the energy development will affect the global issue. It describes how the future energy will be compatible with the sustainable development and the efficient use of energy. Energy scenario gives a clear picture of how the future energy is related with the economic growth and increased GDP [1].

1.1.1 Global Energy Scenario

Global energy council (GEC) scenario drives the world towards a specific objective, such that we can think alternatively for any kind of uncertainty. Energy is one of the major inputs for the economic development of any country. The major sources of energy in the world are oil, coal, natural gas, hydro energy, renewable combustible wastes and other energy sources. The contribution of different energy sources to the total supply of energy in the world are: Oil-35.1%, Coal-23.5%, Natural gas-20.7%, Renewable combustible wastes-11.1%, Nuclear-6.8%, Hydro-2.3% and Other sources-0.5% [2]. World electricity demand is expected to continue more strongly than any other form of Energy. Because electricity is the fastest growing final form of energy and easy to transmit and use. Developing country population growth will be increased up to 90% with in 2030 due to the urbanization, so for this reason main energy demand will be increased automatically [2]. **Figure 1** depicts the final energy consumption growth between the year 1971 and 2013. It is seen from the figure that the final energy consumption has almost been doubled within the period 1971 to 2013. The total world energy demand is assumed to

rise from 505 quadrillion British thermal units (Btu) in 2008 to 619 quadrillion Btu in 2020 and 770 quadrillion Btu in 2035 [3].Such a huge growth in the energy demand will result in fast depletion in the primary energy reserves. Out of total global power demand, coal based thermal power is meeting about 2/3rd of the total requirement. So coal is the world's second largest source of primary energy after oil and is expected to replace oil within few years. A report has shown an estimation of 869 billion tonnes of worldwide reserved coal that could last for 115 years based on the present production rate [4].
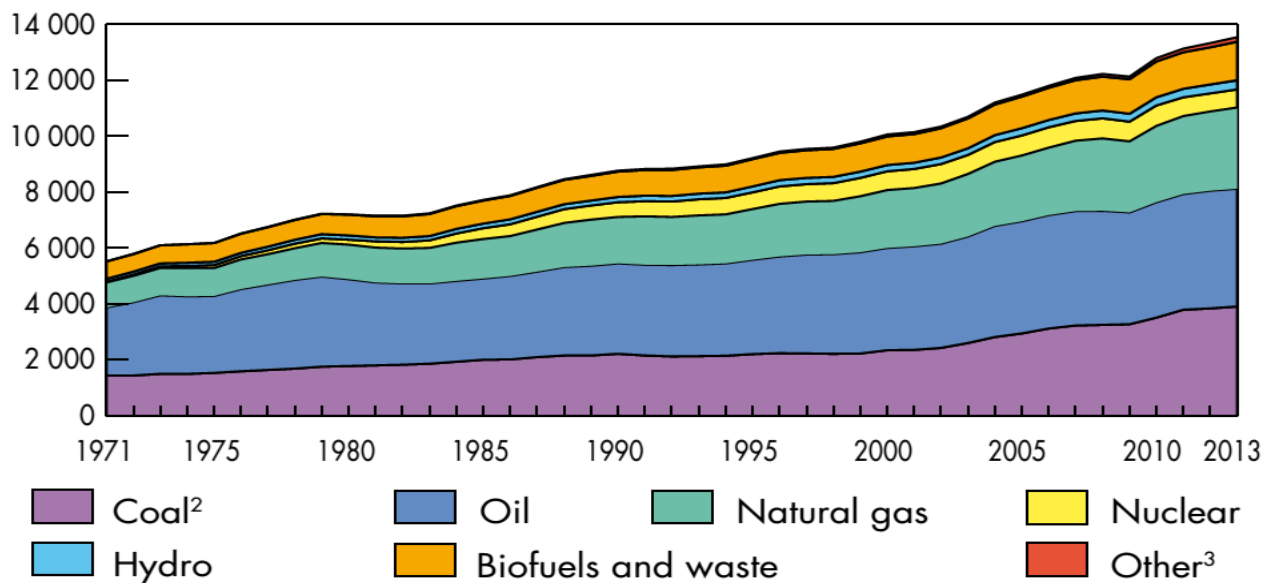
Fig 1: World Total Final Fuel Consumption by Mtoe[1] since 1971 to 2013 [5]

1. 1Mtoe (Million ton oil equivalence) = 4.1868×10^{10} MJ

2. In this figure peat and oil shale are aggregated with coal

3. Includes geothermal, solar, wind, heat etc.

Figure 2 represents that Asia has the largest recoverable reserves of coal followed by Europe and North America. Global consumption of coal is growing and is expected to increase even more with the increase in the energy demand of the developing countries. The introduction of various carbon management schemes, particularly carbon capture and storage (CCS), is vital to mitigate the impact of future coal use on the environment.
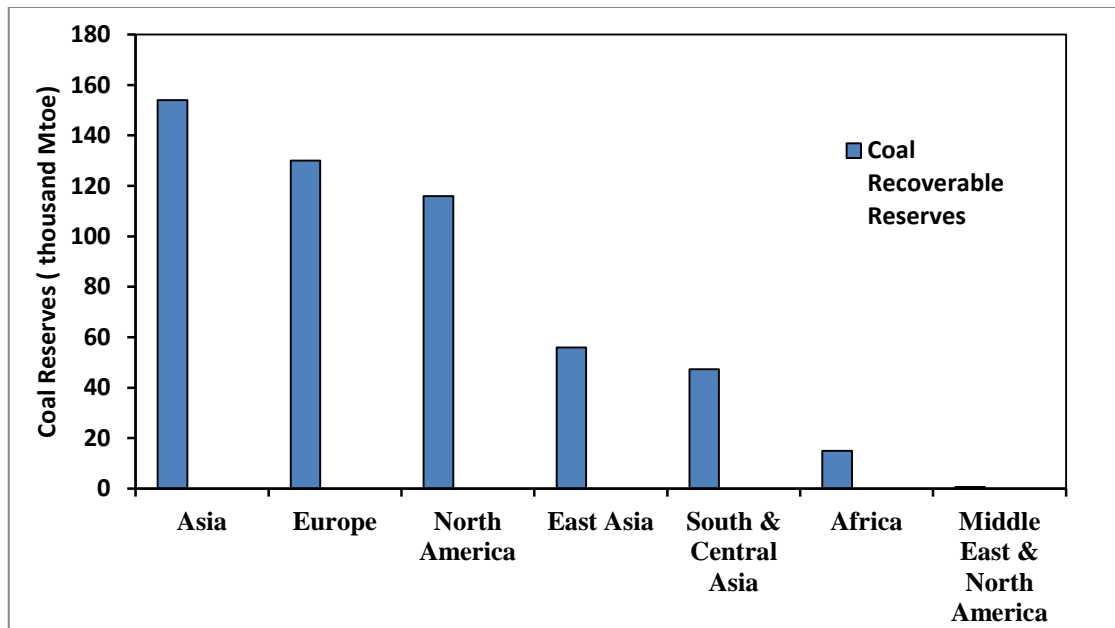
Fig 2: Coal recoverable reserves by region [6]
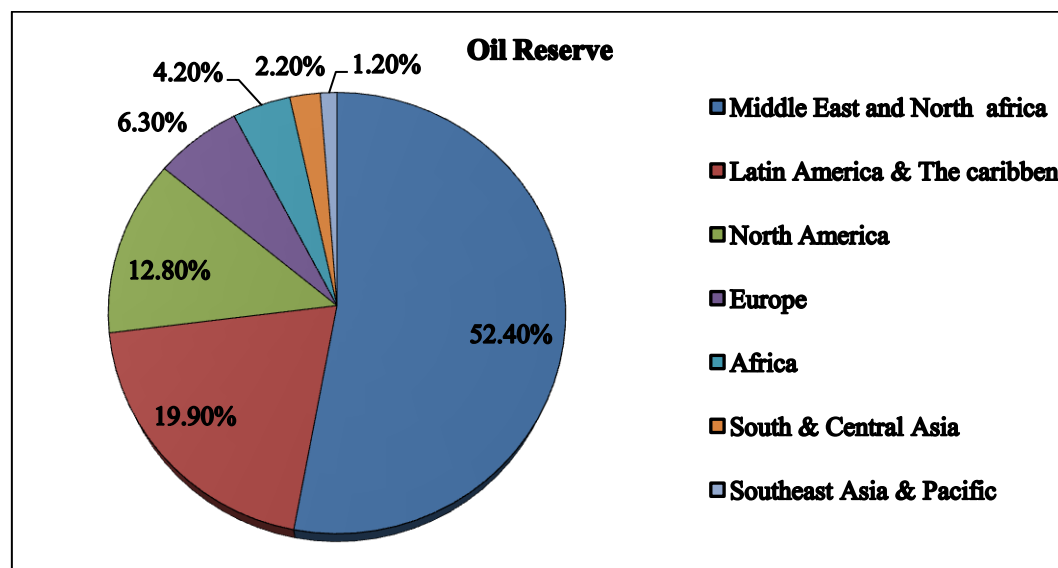
Fig 3: Worldwide Oil recoverable reserves by region [6]

The worldwide consumption of oil has increased by 32%, from 66 Mbd (million barrels per day) in 1991 to 88 Mbd in 2011, with a remarkable increase in reserves of 60% within the same period. The oil reserve at 2011 was 1650 billion barrels indicates the termination of oil resource within 50 years at the same consumption rate of 2011 [4]. **Figure 3** indicates that Middle East & North Africa has the biggest recoverable oil reserve followed by Latin America & the Caribbean.
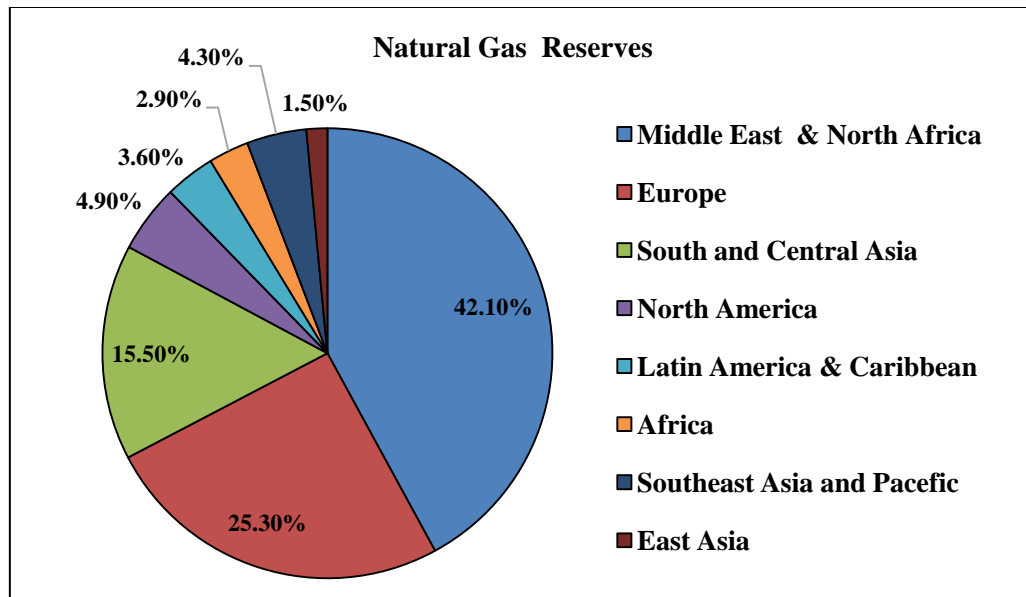
Fig 4: Worldwide Natural Gas Recoverable Reserves by Region [6]

Natural gas is the cleanest and most efficient one of the fossil fuels. For electricity generation, it has low investment costs and offers flexibility. But it is one of the less exploited fossil fuels, and could yet provide a significant contribution to the reduction of greenhouse gas emission. Over 100 countries hold reserves of natural gas, and it is estimated that the global reserve is of 186 trillion cubic meter. **Figure 4** clearly shows that Middle East & North Africa hold the maximum reserves followed by Europe and South and Central Asia.

1.1.2 ENERGY SCENARIO IN INDIA:

India is a country with more than 1.2 billion people accounting for more than 17% of world's population. It is the seventh largest country in the world. India has 28 states and 7 union territories. It faces a formidable challenge in providing adequate energy supplies to users at a reasonable cost. In the last six decades, India's energy use has increased 16 times and the installed electricity capacity increased by 84 times. In 2008, India's energy use was the fifth highest in the world. Nevertheless, India as a country suffers from significant energy poverty and throughout electricity deficits. In recent years, India's energy consumption is being increased at a relatively fast rate due to population growth and economic development [7]. Although new oil and gas plants are planned, but coal is expected to remain the dominant fuel for power generation. In India the demand of electricity is always more than the supply and the coal reserves in India is in better condition than other fossil fuels, thus the power production is totally dependent on the coal, which is responsible to a large extent.
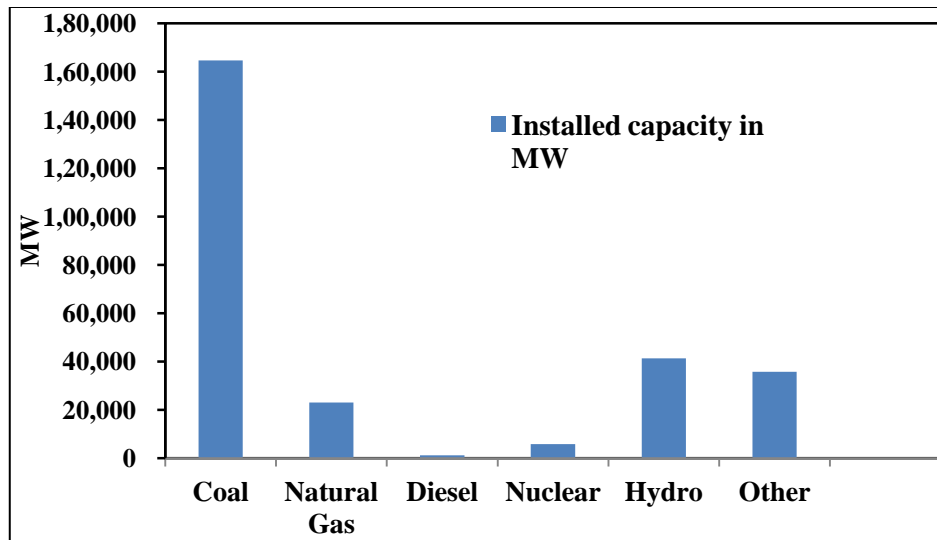
Fig 5: The various energy resources with their respective installed capacity (in MW) in India as per the data on 28-feb-2015 [8]

Figure 5 depicts that installed capacity of coal based power plant for electricity production is very high than other fossil fuels and renewable energy in India. The total installed capacity of electricity generation in India is about 271.772 GW as on the end of February 2015 and generated about 966.777 GW from April 2013 to February 2015. India becomes the third largest country of generation of electricity with 4.8 % global share of electricity by surpassing Japan and Russia. Renewable power plant constitute of 27.80% of total installed capacity and non-renewable consist of 72.20% [8].

Figure 6 represents that increasing energy demand in various sectors. It is evident from the figure that the growth of energy demand is highest for residential sector and energy demand is increasing sharply with time. So for this reason India is struggling with skyrocketing energy demand, declining energy supply and peak load blackout and shortage which limit the energy access. Such a huge growth in the energy demand will result in fast depletion in the primary energy mainly coal reserve. Geological Survey of India has estimated a total reserve of 301.56 billion tonnes of coal in India as on 01.04.2014 of which 5.313 billion tonnes are prime coking Coal, 28.76 billion tonnes are medium and semi-coking coal and 266.00 billion tonnes are non-coking coal **[10]**.
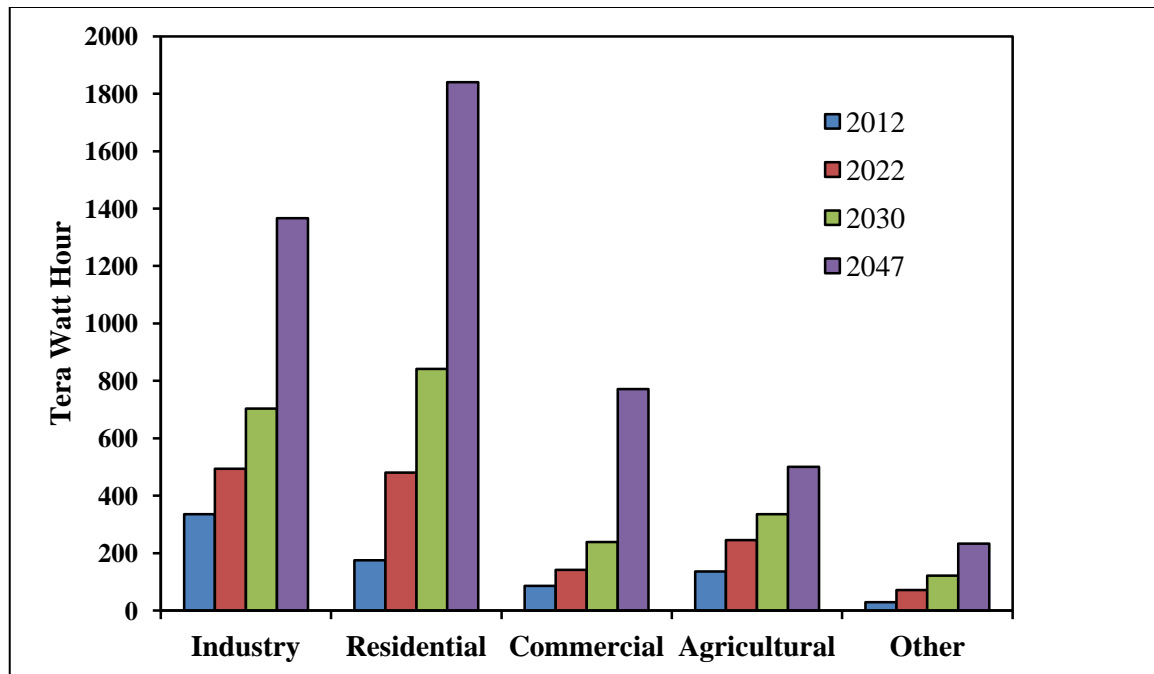
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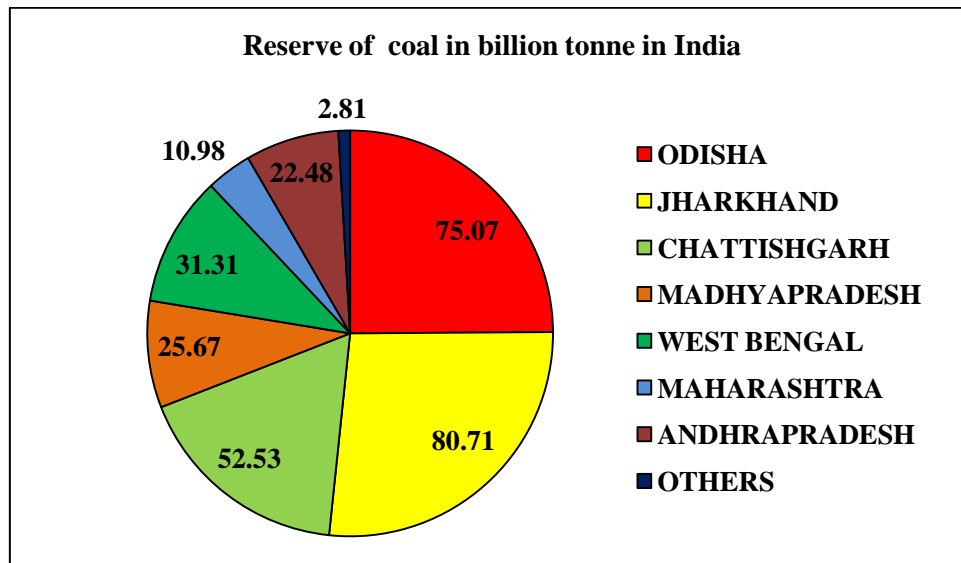
Figure7: State wise Coal Reserve in India as on 01.04.2014 [10]

Figure 7 depicts that the major coal reservoir of India are Jharkhand, Odisha and Chattishgarh. In 2010 due to huge deficiencies of primary fuel like coal and to meet the urgent and growing demand for energy by advancing clean energy solutions, the Government of India's Ministry of New and Renewable Energy launched the Jawaharlal Nehru National Solar Mission (NSM or Mission) in 2010 to promote grid-connected and off-grid solar energy. The Indian government also recognizes that wind energy can be a significant clean energy resource. Supported by initial

government policies, India is already the fifth-largest wind energy producer, achieving 20 Giga watts (GW) of installed wind power. Yet, much more can be achieved. India's wind energy production can grow at least four to five times its current level to achieve the country's 100 GW wind energy potential. To achieve the higher potential, the government announced plans in 2014 to launch a National Wind Energy Mission [**11,12].**

1.1.3 Economics related to energy intensity:

Energy intensity is a measure of Output of an economy in relation to per unit consumption of power. It is known that the energy consumption is proportional to the size of economy. So normally higher the size of economy, higher the energy consumption. The primary energy intensity relates the total energy consumption of a country to its GDP. The primary intensity measures how much energy is required to produce one unit of GDP. It is obvious that it's better to keep energy consumption at minimum by adopting energy efficient technologies. This is also an important part of economy because it calls for maximum output by consuming minimum resources. This will reduce electricity bill of households, industry and government. It will also save disproportionate investment of capital in power sector which could be used in other sector. Energy has also environmental cost. So not saving energy is very much dangerous. Saving energy results in avoiding emission of millions of tons of greenhouse gases annually. Different countries have different energy intensity and it's depend upon various factors such as technology, share of particular sector in economy, Government's investment in power sector **[13].**

Figure 8 represents variation in primary energy supply with year of different countries. We can see from **Figure 8** that India's energy intensity has come down rapidly in past couple of decades and this fall continues. This is mainly because of the following reasons [**13**]:

- LPG reforms in 1991 made private sector the dominant player in the economy. In pre-LPG era there was lack of efficiencies in LPG production. But private sector have to compete and continuously improve itself to lower the cost of LPG to remain competitive. Indians buy one of the most expensive power globally and this is even truer if we compare per capita income with per capita energy costs. This has to force consumers to keep their consumption low be in industry or house hold and for this reason per capita consumption is very much low in India.
- Another reason is for low energy intensity in India because of higher energy consumption in manufacturing sector.
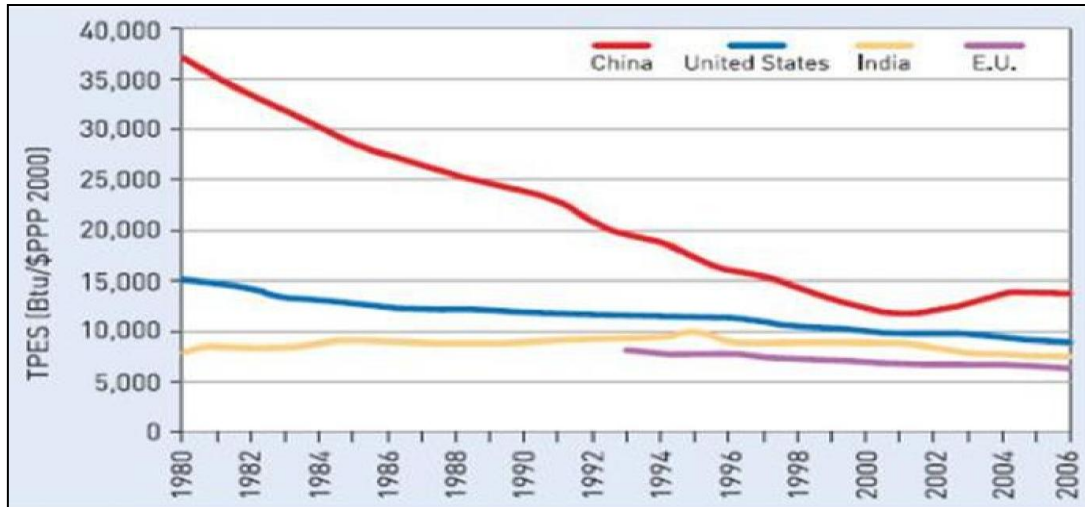
Fig 8: Variation of economy wide energy intensity [13]

1.1.4 Future Consumption of energy:

Mainly in the **figure 9** we see a strong growth of renewable energy. The BP Report shows strong growth in renewable energy, but it will be only about 8% of global energy supply by 2035 [**14**].
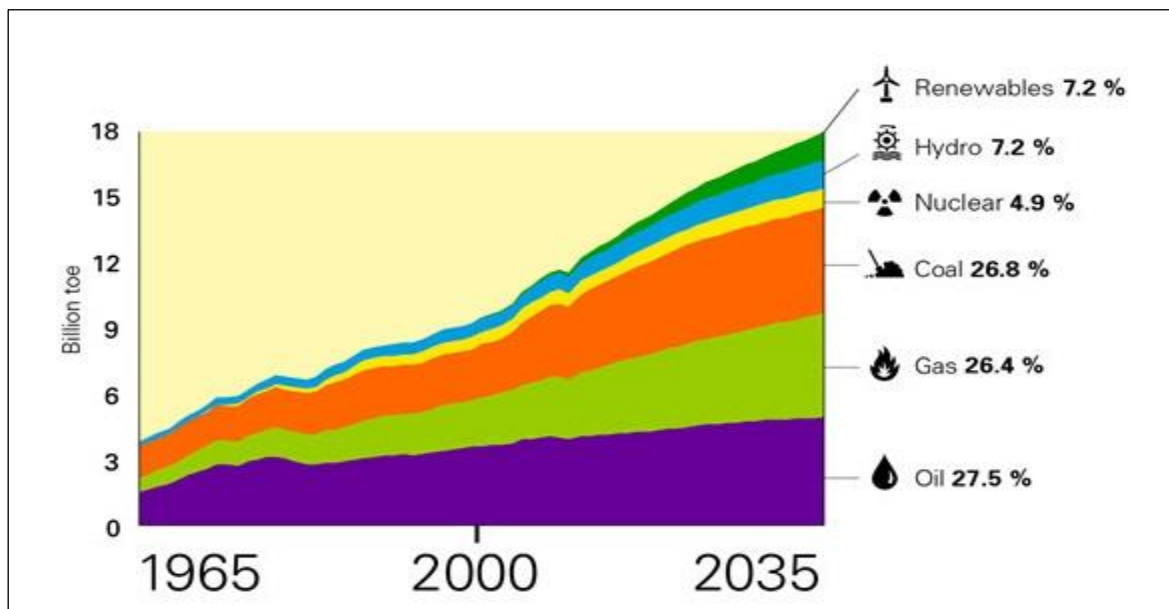
Fig 9: Future Consumption of Global Energy up To 2035 Resource Wise [15]

World energy council (WEC) drives the world towards a specific objective such that we can think alternatively if any kind of uncertainty comes. WEC present two types of energy scenario up to 2050. These are Jazz and symphony.

- According to the energy scenario JAZZ focus on energy equity with priority given to achieving individual access and affordability of energy through economic growth.
- According to the symphony it focuses on achieving sustainable development through internationally co-ordinate policies and practice.
- Due to this ever increasing economic growth rate it is quite difficult to meet such energy demand. The WEC has estimated that total primary energy supply (equal to consumption) will increase globally from 546 EJ (151 PWh) in 2010 to 849 EJ (144 PWh) in JAZZ scenario and 696 EJ (193 PWh) in symphony scenario [1]. This corresponds to the increase in 61% in JAZZ and 27% in symphony. According to this scenario total global primary energy consumption will be increased by 45%.

1.1.5 The change in primary energy supply in different region from the year 2010 to 2050:
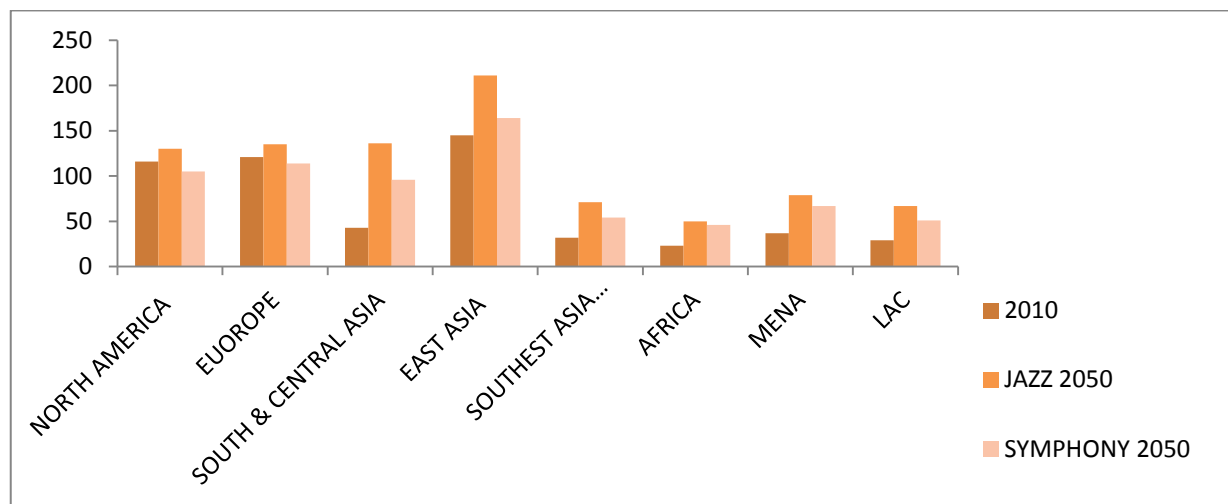
Fig 10: Primary energy consumption in different region by 2050 [1]

Figure 10 depicts that the energy intensity according to both the scenarios changes to 4.4 and 4.1 in 2050 from 8.8 in 2010. The future energy mix in 2050 shows that growth rate will be highest for renewable energy sources. In absolute term fossil fuel will remain dominant up to 2050. The share of fossil fuel will be 77% in JAZZ and 59% in symphony compare to 79 % in 2010. The use of renewable energy sources will increase from 15 % in 2010 to almost 30% in 2050. To meet the future

demand and to maintain the compatibility with ever increasing economic growth rate the electricity generation have to increase from 21.5 billion MWh to 53.6 billion MWh i.e. about 150% [1].

1.1.6 Scope of Future Investment in Electricity Generation:

The adjusted prices in the electricity market across the OECD countries increased by 2.8 % in households and 5.3% in industrial user between 2006 and 2013. Between now and 2040 electricity prices will be increased by 57% in EU and 50% in US due to the higher operational, maintenance, investment cost. About $3 trillion has been already invested between 2000 and 2012 and a further $7.6 trillion require to be invested in the near future 2040. This high level investment will need to continue if the energy policy needs to be met. Investment need in conventional, renewable, centralized, decentralized will be $180 billion annually and in expansion, modernization, installation of transmission and distribution grid will be $100 billion per year [16]. To meet the huge energy demand in future India's electricity sector has already utilized renewable energy specially the wind energy. As on 31st January 2014 India's total installed capacity 31.15 GW on non-conventional renewable technology based electricity. In this context the various renewable energy resources in India and their installed capacity are as follows:

Table1: Installed capacity of renewable energy sources in India [17]

Type	Technology	Installed capacity (MW)
Grid connected power	Wind	23,444 (Gujarat highest 10600 MW)
"	Small hydro	4055.36
"	Bagasse cogeneration	3008.35
"	solar	3743.97
"	Biomass power gasification	1410.20
"	Waste to power	115.08
"	Total	35,776.96
Off grid connected power	Biogases Cogeneration	591.87
"	SPV system	234.35
"	Biomass gasified-industrial	152.05
"	Waste to power	154.47
"	Biomass gasified-rural	17.95
"	Water mill / micro hydro	17.21
"	Aero generator hybrid system	2.53
"	Total	1170.43

1.1.7 Advantages of Using Renewable Resources:

The use of the conventional energy resources is making unfriendly impact on the environment. The burning of fossil fuel such as coal, oil, natural gas for generating electricity will release greenhouse gases and other pollutant into the atmosphere and will impose the following impact to the earth and mankind.

Global warming and Climatic Change

The atmosphere is a thin layer of gases which surrounds the earth. The two most important layers in the atmosphere are known as the troposphere and the stratosphere. 90% of all the molecules in the atmosphere are in the troposphere. The atmosphere is composed mainly of 21% Oxygen, 78% Nitrogen, 0.04% Carbon dioxide and argon 0.04% by volume. The earth is surrounded by a blanket of gases including greenhouse gases. The greenhouse gases are those gases in the atmosphere which by absorbing thermal radiation emitted by the earth's surface have a blanketing effect over the surface keeping it warmer than it would otherwise be. This results in buildup of energy, and the overall warming of the atmosphere. This blanket traps energy in the atmosphere, much the same way as glass traps heat inside a greenhouse. This warming of the earth is called greenhouse effect.

With the economic growth, the greenhouse gas (GHG) emission has also increased, resulting a change in climate. CO_2 is the most emitted gas among GHGs. The concentration of CO_2 was 396 ppmv on 2013, 40% higher than in the mid - 1800s with an increase in 2ppmv/year in the last 10 years [18]. Significant increase in the level of methane (CH_4) and nitrous oxide (N_2O) have also happened. This type of greenhouse gases are produced mainly due to human activities of energy production (electricity).

Global Emission by Gas:

At the global scale, the key greenhouse gases emitted by human activities are represented in **Figure 11**. The emission of those gases are [**19**]:

- **Carbon Dioxide** - Fossil fuel use is the primary source of CO_2. The way in which people use land is also an important source of CO_2, especially when it involves deforestation. CO_2 can also be emitted from land clearing for agriculture, deforestation etc.
- **Methane (CH_4)** –Agricultural activities, waste management, biomass burning etc.

- **Nitrous oxide (N₂O)** - Agricultural activities, such as fertilizer use, are the primary source of N_2O emissions.
- **Fluorinated gases (F-gases)** - Industrial processes, refrigeration, and the use of a variety of consumer products contribute to emissions of F-gases, which include hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF6).
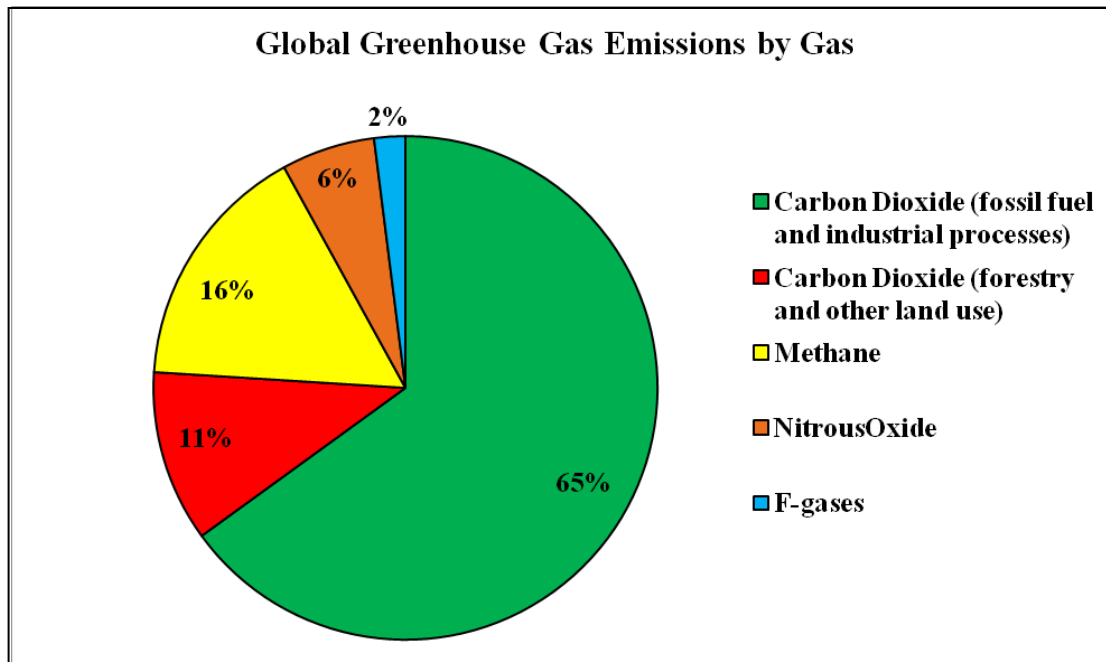
Fig 11: Global Greenhouse Gas Emissions [19]

Global Emissions by Economic Sector:

Global greenhouse gas can also be emitted by the economic activities that lead to their production. **Figure 12** depicts those various economic sector which are the main source of greenhouse gases.

- **Electricity and Heat Production:** 25% of total greenhouse gas is emitted from this source like the burning coal, oil, natural gas for electricity and heat is the largest single source of global greenhouse gas emissions.
- **Industry:** Greenhouse gas emissions from industry primarily involve fossil fuels burned on-site at facilities for energy this sector can produce 21% of total green house gas.
- **Transportation:** Greenhouse gas emissions from this sector primarily involve fossil fuels burned for road, rail, air, and marine transportation. For this reason mainly there is a huge potential of using biofuels instead of fossil fuels. 14% of total greenhouse gas is produced from this sector.

- **Agriculture, Forestry, and Other Land Use:** Greenhouse gas emissions from this sector come mostly from agriculture (cultivation of crops and livestock) and deforestation. This estimate does not include the CO_2 that ecosystems remove from the atmosphere by sequestering carbon in biomass, dead organic matter and soils, which compensate approximately 20% of emissions from this sector.
- **Buildings and other energy**: Production of greenhouse gases form this sector is mainly due to the cooking in home, fuel extraction, refining, processing etc.

Greenhouse Gas Emissions by Economic Sector

- Electricity and Heat Production — 25%
- Agriculture, Forestry, and other land use — 24%
- Industry — 21%
- Transportation — 14%
- Other Energy — 10%
- Building — 6%
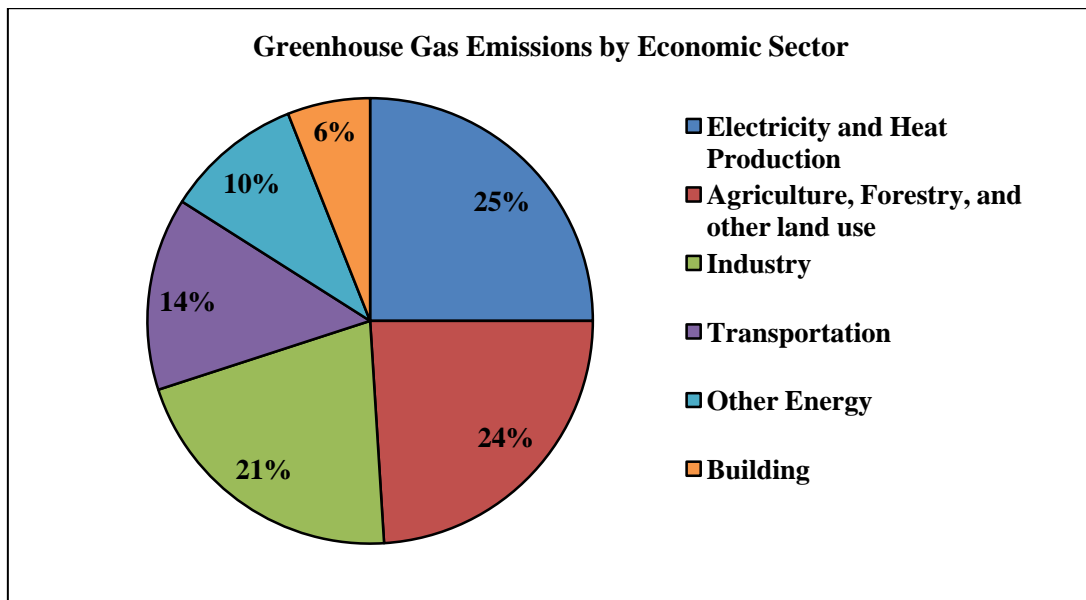
Fig 12: Global Greenhouse Gas Emissions by Economic Sector [19]

Figure 13 represents a trend of total carbon emissions in million metric tons .carbon emissions from fossil fuels have significantly increased since 1900 [**19**].
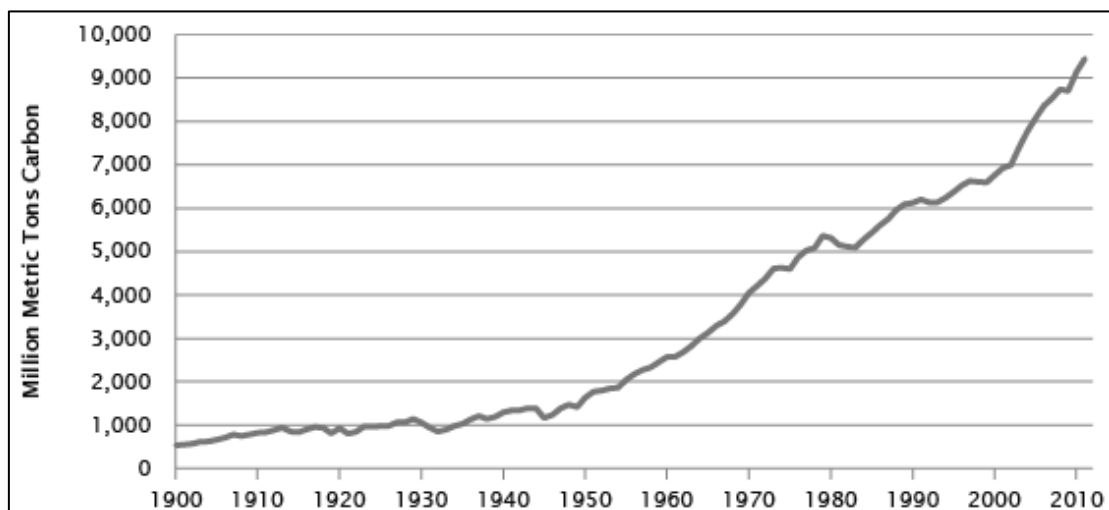
Fig 13: Trend of Global Carbon emissions from Fossils Fuels [19]

Since 1970, CO_2 emissions have increased by about 90%, with emissions from fossil fuel combustion and industrial processes contributing about 78% of the total greenhouse gas emission increase from 1970 to 2011. Agriculture, deforestation, and other land use changes have been the second-largest contributor.The consequence of global warming has far reaching impact on our ecosystem affecting the agricultural production causing rising in the sea level and effect on the young children and the aged and as well as the people with chronic health problem.

Obstacle in Economic development

Fossil fuel reserved has their limit. Over the past decade we have rapidly depleted these limited natural resources. The shortage of the fossil fuel in the not too distant future could affect the activities of all walk of the life and delay in economic development. This could result in the global degradation of people's living standard. The only solution to this problem is the clean energy.

Clean energy includes demand and supply-side resources that meet energy demand with less pollution than that created by conventional, fossil-based generation. Clean energy resources include:

Increased Energy Efficiency - Using less energy to provide the same or improved level of service to the energy consumer in an economically efficient way. Energy efficiency measures include a wide variety of technologies and processes, can be implemented across all major energy-consuming sectors, and may affect all energy sources (e.g., natural gas, electricity, etc).

Renewable energy – Energy generated partially or entirely from non-depleting energy sources for direct end use or electricity generation. Renewable energy definitions vary by state, but usually include wind, solar, and geothermal energy. Some states also consider low-impact or small hydro, biomass, biogas, and waste-to-energy to be renewable energy sources. Renewable energy can be generated on site or at a central station.

Clean distributed generation – refers to small-scale renewable energy and CHP at the customer or end-use site [20].

Clean energy — wind, solar, geothermal, hydroelectric, and biomass — provides substantial benefits for our climate, our health, and our economy. Renewable electricity generation from biomass can have a wide range of global warming emissions depending on the resource and how it is harvested. Sustainably source biomass has a low emissions footprint, while unsustainable sources of biomass can generate significant global warming emissions.

1.1.8 Impact of renewable energy on human health [21]:

Generating electricity from renewable energy rather than fossil fuels offers significant public health benefits. Climate scientist have observed that CO_2 concentrations in the atmosphere have been increasing significantly over the past century. The concentration of CO_2 in 2013 is 40% higher than in the mid-1800.The rise of greenhouse gases has increased the global mean temperature. The rise in temperatures has implications for life and human health. According to the World Health Organization, potential risks to health include deaths from thermal extremes and weather disasters, a higher incidence to food related, photochemical air pollutant and conflict over depleted natural sources [**22**]. **Table 2** lists the main diseases which are produced due to climate change:

Table 2: Introduction of various diseases due to climate change

Diseases	Effect of Climate Change on Health
Asthma, Respiratory allergies and airway diseases.	The global rise in asthma and other respiratory problem are indirectly related to climate change,
Cancer	Climate change is expected to increase heavy precipitation and flooding events, which may increase the chance of toxic contamination and depletion in ozone layer will result in increased UV radiation which increase the risk of skin cancer.
Cardiovascular disease and stroke	Climate change can create many cardiovascular diseases due to extreme hot and cold atmosphere condition.
Food borne Diseases and nutrition	Climate change may impact rates of food borne illness through increased temperature.
Heat-related diseases	Many diseases like heat cramp heat stroke are related to climate change.
Human developmental effects	Climate change will lead to changes in agricultural practices that might increase pesticide use. Which may effect on fetal loss, child growth and male reproductive development.

To avoid this adverse impact of climate change, it is necessary to limit the rising global temperature and carbon emission by using renewable sources for energy production.

So using renewable sources like biomass for energy extraction is more popular than fossils fuel. Because it emits small air pollutants, which are generally much lower than coal- and natural gas-fired power plants. Fuel from various biomass is an alternative source of transportation fuel, which can reduce carbon emission sharply in atmosphere. Because of improvements in biotechnology, bioethanol produced from biomass has become a sustainable source of liquid fuel.We can produce various gases like H_2, Syngas, from biomass used as an alternative transportation fuel.

1.1.9 Environmental Impacts of Renewable Energy Technologies [23]:

All energy sources have some impact on our environment. Fossils fuels, coal, oil and natural gas do more harm than renewable energy sources by most measures, including air and water pollution, damage to public health, wildlife and habitat loss, water use, land use, and greenhouse gas emissions. It is still important to understand the environmental impacts associated with producing power from renewable energy sources such as wind, solar, geothermal, biomass, and hydropower.

Power production from wind is one of the cleanest and most sustainable ways to generate electricity because it produces no toxic pollution or global warming emissions. Wind is also abundant and affordable which makes it a viable and large-scale alternative to fossil fuels but wind energy also have some environmental impact on public health and community, wildlife. Also huge land is required for wind plant.

The environmental impact associated with solar power can include land use, water use and the use of hazardous materials in manufacturing solar equipment. Though the types of impacts vary greatly depending on the scale of the system and the technology used — photovoltaic (PV) solar cells or concentrating solar thermal plants (CSP).

Biomass is one of the popular renewable resources for energy production. But the production of biomass feedstock can create environmental impact. Because production of huge amount of energy crops produce greenhouse gases and affect our ecosystem.

Hydroelectric power includes both massive hydroelectric dams and small run-of-the-river plants. A huge quantity of land is required and can produce impact on wild life. This type of power plant can create huge impact on the river ecosystem.

However generating electricity from renewable resources have lower impact on public health as compared to conventional resources. Renewable energy is also providing affordable electricity across the country right now, and can help stabilize energy prices in the future. The costs of renewable energy technologies have declined steadily, and are projected to drop even more. For example, the average price of a solar panel has dropped almost 60 percent since 2011 and the cost of generating electricity from wind dropped more than 20 percent between 2010 and 2012 and more than 80 percent since 1980 [**24**].

Only the installation cost is quite high for renewable plants but once built they operate at very low cost i.e. the running cost is low as for most technologies, the fuel is free. As a result, renewable energy prices are relatively stable over time. **Figure 14** represents cumulative electricity and natural gas savings for consumers in all sectors of the economy. The savings would reach $64.3 billion by 2025 and would grow to $95.5 billion by 2030 [**25**].
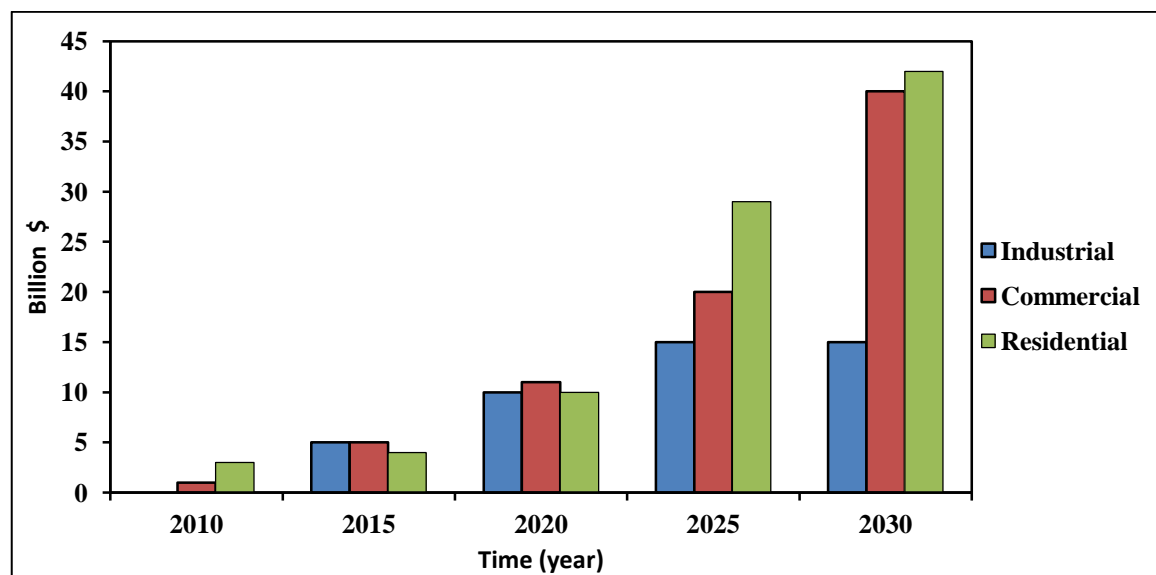
Fig14: Electricity and natural gas bill saving by various sector (billion $) [26]

1.1.10: Recent market and industry trends of Renewable Energy sources:

In our system mainly we use conventional energy. We receive this type of energy from Coal, Oil but due to increment of urbanization, demand of energy is increasing sharply and due to the limited resources like Coal, Oil, we can't depend on those types of resources only. For Sustainable development of our society we should use renewable energy.

These types of energy we get from clean sources which have much lower environmental impact. Renewable energy source cannot be finished like other conventional sources. Due to increasing of population energy demand uplifted gradually thus energy import increases which is very costly, but by using Renewable energy we can produce clean energy within the nation, so huge energy money can be saved for local economic and creating job prospect in a nation.

Biomass Energy:

Bio-heat production remained stable in 2014, increasing 1% over 2013 [27]. Global bio-power production increased approximately 9%, with China, Brazil, and Japan leading for capacity additions, and the United States and Germany leading for generation. Liquid biofuel production increased by 9% in 2014, reaching its highest level till date. Mainly United State and Brazil dominated overall volume. Asia also experienced high production growth rate particularly in production sector [27]. India is very rich in biomass. It has a potential of 19500 MW biomass energy. Which includes 3500 MW from bagasse based cogeneration and 16000 MW from surplus biomass. Currently India has 537 MW for commissioned and 536 MW under construction [28]. The majority of transport related policies has been continued to focus on the biofuel sector and on road transport. Various policies have been taken related to linkage between electrical vehicle renewable sources. As of early 2015 biofuel blend mandates were placed in 33 countries.

Geothermal Energy:

For producing an estimate of 74 (TWh) renewable energy 640 MW of new geothermal energy had been commissioned in 2014. Kenya is the largest production of new geothermal energy. An estimated 1.1 gigawatts-thermal (GWth) of geothermal direct use (heat) capacity was added in 2014. Over the past five years, total power capacity has grown at an average annual rate of 3.6%, and heat capacity at an estimated 5.9%. [27].

HydroPower:

The total global hydropower capacity has been increased to approximately 1,055 GW in 2015. China has installed most capacity of 22 GW hydro power in recent year. The demand of hydropower has increased due to the continued innovation of industry towards ever-more flexible, efficient, and reliable facilities. The development of wind power in India began in the 1990s and has significantly increased in last five year. Many domestic policies support for wind power has led India to become the country with the fifth installed wind power capacity in the world. Wind power generates 1.6% of the total country's power.

Solar Power:

Solar power can produce tremendous amount of power every day. Solar PV is also starting to play a substantial role in electricity generation in some countries because of rapidly falling cost of PV cell. Due to this cost decrement, generation of electricity from solar has made a huge competition with fossils fuel. Recently various projects of solar energy have been started in India. Rajasthan is one of the state of India in the field of solar energy. The total photovoltaic capacity had passed 500 MW in Rajasthan. There are various projects have been started related to solar power production. It is one of a large numbers of solar parks expected to be built in 35000 km^2 area of Thar desert that has been reserved for solar power projects. Also the Canal solar project is a project launched in Gujrat to use 19000 kilometer long network of Narmada canals across the state for setting up solar panels to generate electricity [28].

However, the advancement of the developing nations in renewable energy is not only bounded within China. In 2014, Brazil ($7.6 billion), India ($7.4 billion) and South Africa ($5.5 billion) were all in the top 10 list of investing countries. From this perspective, India has achieved about 4089.18 MW grid connected renewable energy generation in the fiscal year 14-15 and about 93.16 MW_{EQ} off grid. Muppandal wind farm in Tamil Nadu has the highest generation capacity is about 1500 MW. [29].

According to UNEP (United Nation Environmental Programme) in the year 2014 the green energy investment is about $270 billion. China is the highest investor in the renewable energy, creating a record of $83.3 billion, 39% more from 2013, United State is the second $38.3 billion, 7 % more from 2013 and Japan is the third $35.5, 10% more from 2013 [30].

By the end of 2014, China, The United States, Brazil, Canada, and Germany remained the top countries for total installed renewable power capacity; the top countries for non-hydro capacity were again China, The United States, and Germany, followed by Spain, Italy, and India. Among the world's top 20 countries for non-hydro capacity, Denmark had a clear lead for total capacity per capita. Uruguay, Mauritius, and Costa Rica were among the top countries for investment in new renewable power and fuels relative to annual GDP [31].
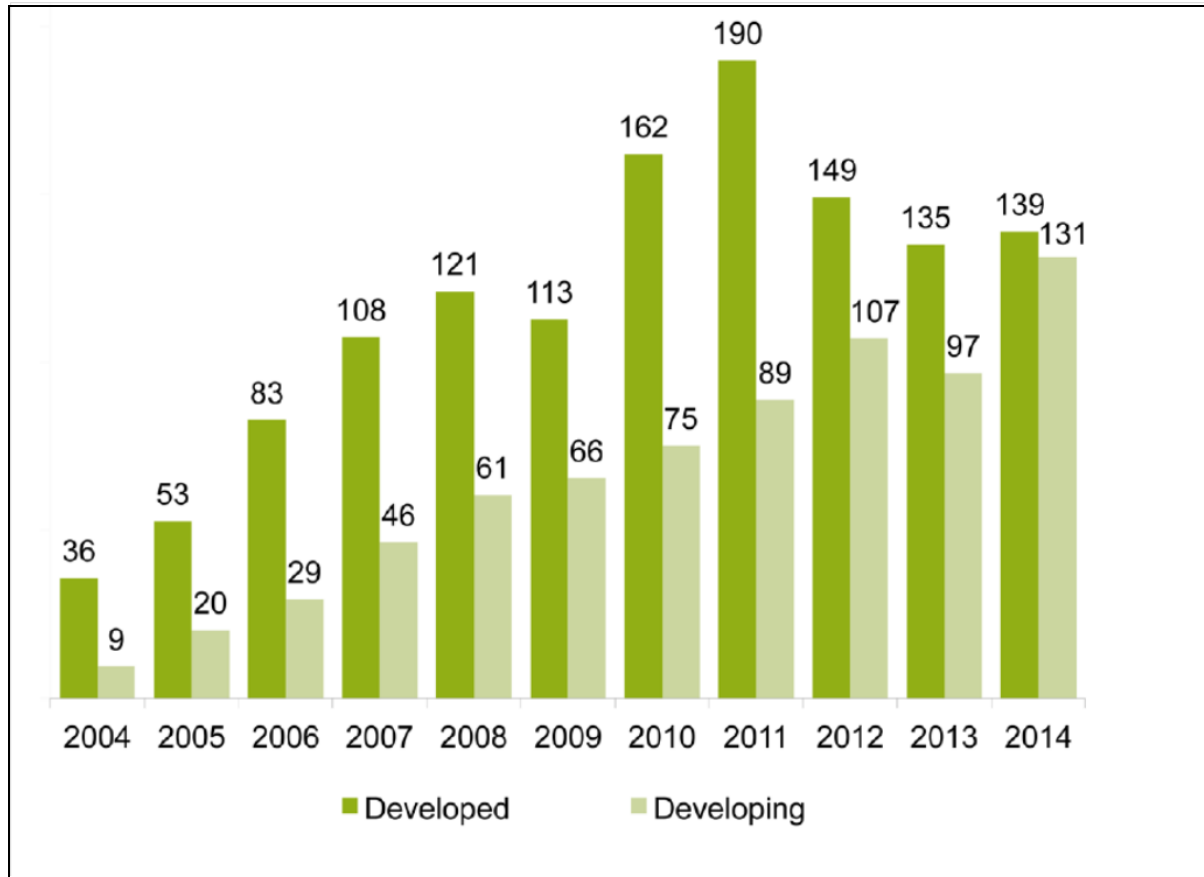
Figure15: Sector wise global investments ($BN) in renewable energy from 2004-2014[32]

Figure 15 shows that the difference in investment between developed and developing countries was more equal than ever before in 2014. Developing countries have increased their investment in renewable energy almost in a straight line since 2004 while there is a single drop in 2013.

1.2 Importance of biomass energy in the present context:

Renewable/sustainable energy options include hydroelectric, biomass, wind, solar, geothermal and ocean tides and currently represent about 8% of total U.S. energy consumption [**33**]. Biomass was the major energy source for mankind before the discovery of fossil fuels, and declined from meeting over 70% of the world's total energy demand in 1860 to only about 7% in 1990 [**34**]. In 2010, approximately 48% of U.S. renewable energy was from biomass, but half of it was via traditional biomass that generates heat by combustion. The energy extract from biomass is mainly produced by photosynthesis process .This energy is called renewable energy because carbon dioxide and water contained inside plants and animals are released back in to the atmosphere when they are

burned and we can grow more plants and crops to create biomass energy. Among the other renewable energy resources the using of biomass energy become increasing day by day. Another upcoming use of biomass is production of Hydrogen Gas which is treated as an alternative clean transportation fuel [35].Resources of biomass are widely spread all over the world in various form. They may be forest products agricultural wastes, municipal wastes or animal wastes or byproducts of certain fruits like switchgrass which have been sufficient higher calorific value [36]. **Figure 16** shows different countries across the world with their biomass capacities in 2011.which has been shown that Europe has largest biomass capacity of 26.2GW[37].There is huge potential for bio fuels, Biomass Energy production in India because of avability of various Sources like agri-wastes, animal wastes, and municipal wastes are present in India. Earlier wood was the main bio fuels used in India. But now due to scarcity of wood, people in rural area are moving in to alternating resources like the agricultural wastes, forest residue for extracting bio fuels [38].
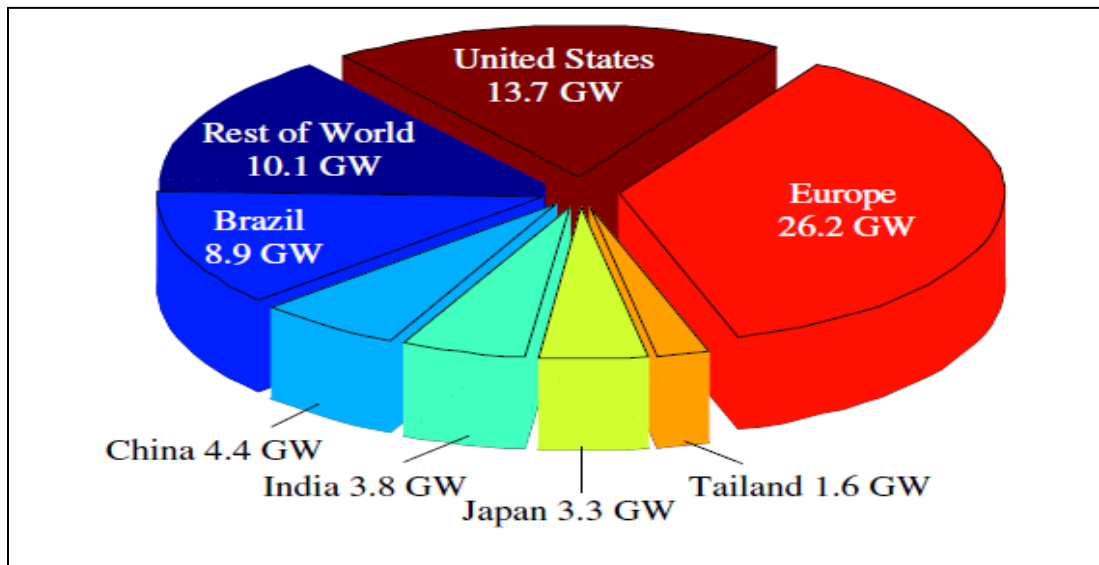
Fig.16: Global biomass power capacity in 2011[38]

Today our transportation sector are totally depend on petroleum based fuel like petrol, Diesel, Natural gas etc. This transportation sector mainly consume 60% of total oil consumption in world [39].This transportation section emits total 70% of global CO production and 19% of global CO_2 production which is harmful for our environment and enhance global warming effect [40].Due to our growing economy vehicle numbers from heavy vehicle to light vehicle are increasing day by day. So for this reason automatically this growth will affect our global climate, global oil reserve and force to change our ecosystem. But now a day's increasing of petroleum fuel prices, increasing concern about global warming effect are forcing to search for new alternative transportation fuel which must be

ecofriendly, huge availability in environment and economically acceptable. Due to improvements in biotechnology there are various biofuels have been proposed like bioethanol, biodiesel, methanol, hydrogen, boron etc. **Figure 17** shows that biofuel are obtained through the transformation of natural aliments, crops, trees.
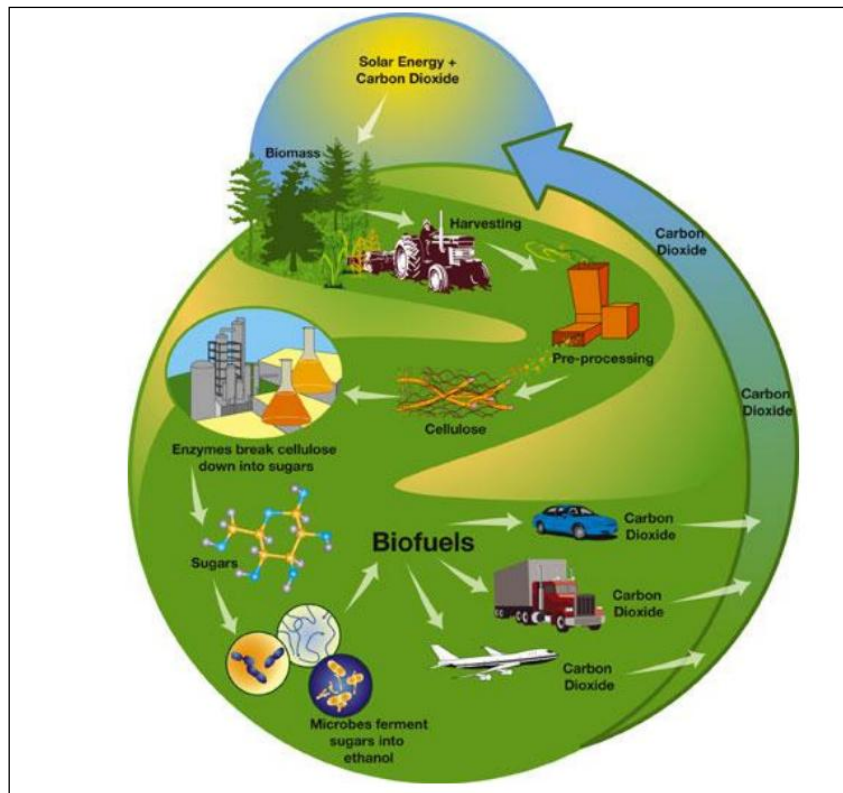
Fig.17: Biofuels and Carbon dioxide cycle [41]

The use of natural material as fuel is said to be harmless for the atmosphere, because its CO2 balance is null. The CO2 released by the combustion of your biofuel is compensated by the absorption of CO2 when your crops or trees grow.

1.2.1 Alternative Technologies for Bio energy Extraction:

Biomass can be converted into useful forms of energy using a number of different processes which are totally depend on the difference type of biomass, end-use requirement, and different form of energy. Biomass can be derived from the cultivation of dedicated energy crops, forest residue and biomass wastes such as sludge from organic industrial waste, municipal waste etc. Conversion of biomass to energy there are mainly three processes: thermo-chemical, bio-chemical, and mechanical extraction [**42**].In case of thermo chemical conversion mainly four process are available:

Combustion, Pyrolysis, Gasification and Liquefaction. Fermentation and Digestion are major process for bio energy extraction in bio-chemical route. In thermo chemical conversion process combustion is one of the most popular process for heat generation.The burning of biomass in air, which is called combustion, is used over a wide range of outputs to convert chemical energy stored in biomass into heat, mechanical power, or electricity using various items of process equipment, mainly stoves, furnaces, boilers, steam turbines, turbo-generators, etc. Combustion of biomass produces hot gases at a temperature around 800–1000°C. It is possible to burn any type of biomass but in practice combustion is feasible only for biomass with a moisture content<50%,unless the biomass is pre-dried. High moisture content biomass is better suited to biological conversion processes. Mainly woody biomass burns into CO_2 and H_2O and produce huge heat. The scale of combustion plant range is mainly in the range of 100MW-3000MW. Heat loss is very much high in this process Net energy efficiencies of this process is very much poor range from 20%-30% [42].

In case of Gasification process mainly consists of partial oxidation and sub-sequent reduction reactions. Mainly this process produces Syngas which mainly consist of hydrogen, carbon monoxide, carbon dioxide, water, methane and higher hydrocarbons (tar).The gasification of biomass can be done using air, oxygen or steam as the gasifying agents. While air based gasification results in adulteration of the syngas with high percentage of nitrogen [43].Gasification unit can be combined with gas turbine and convert gaseous fuel in to electricity. We can use clean fuel before being combusted in the turbine, so we can use more compact and less costly gas cleaning unit. The production of syngas from biomass allows the production of methanol and Hydrogen gas. Which may be used as clean fuel for transportation in future. But transportation of gaseous fuel is very much difficult and preserving cost of gaseous fuel is very much high.

Pyrolysis is conversion of biomass to solid, liquid (bio fuels, bio crude), gaseous form by heating the biomass in the absence of air to around 500°C. Pyrolysis can be used to produce bio oil by converting biomass. This oil is mainly used in engine and turbine. But this oil has poor thermal stability and corrosivity. [42].

Now there is an another route for bio energy production is the biochemical process.Biochemical route are less energy intensive then thermo chemical but require large volume due to low bio energy production [44 45].Two main process in the bio chemical conversion are Fermentation and Anaerobic digestion.Fermentation is one of the most popular method in biochemical conversion category for production of Ethanol. In India due to plenty of sugar crops(sugar cane, sugar beet),starch crops(maize, wheat) this process has huge possibility for clean energy production. After

collecting biomass the starch is converted in to sugar by enzymes, with yeast then converting the sugars to ethanol. Due to the abundant of lignocelluloses biomass such as (wood, grasses) are more used as a feedstock for production of ethanol [42].Anaerobic digestion is mainly series of biological process in which microorganisms break down to biodegradable material in the absence of oxygen. One of the end products is biogas, which is combusted to generate electricity and heat, or can be processed into renewable natural gas and transportation fuels. A range of anaerobic digestion technologies are converting livestock manure, municipal wastewater solids, food waste, high strength industrial wastewater and residuals, fats, oils and various other organic waste streams into biogas, 24 hours a day, 7 days a week. The mixture of this biogas mainly methane andCO_2,with small quantity of other gas. This type technology is mainly used in high moisture content biomass of 80%-90%.Production of biogas is directly used in gas turbine for electricity production or can be upgraded to natural gas by removal of carbon dioxide.

From this various alternative bioenergy extraction processes various biofuels like (biogas, bio diesel, bioethanol, bio-syngas, bio oil, bio hydrogen) are produced. This biofuel is generally refer for electricity production but mainly biofuel is normally used in transportation sector. Fermentation process is the most efficient process for bio fuel production. This type of renewable fuels create huge attention in transportation sector because its availability, reduction of carbon emission and due to low cost. Among them mainly Ethanol is one of the most popular Biofuel. The use of ethanol was tremendously high in Europe and united states until the early 1900s.But production cost of ethanol became very much high after World War II than petroleum fuels. For this reason potentiality of bio ethanol was largely ignored until the incident of oil crisis happened on 1970s [46]. After this mainly interest of bio ethanol production and application as a transportation fuel became increasing. Bio ethanol is renewable fuel for motor vehicles. There are some advantages of bioethanol over other biofuels [47]:

- It is Renewable and produce from fully sustainable resources.
- It is less polluting then Gasoline.
- **Figure 18** depicts that the most important aspect is that CO_2 released by the combustion of ethanol has been fixed by recently growing plant .So this greenhouse gas makes no impact on global warming of environment.
- Fuel ethanol can be blended directly into gasoline and used by vehicles without modifying their engine. So it can be used as reducing carbon emission agent of any type of engine.
- It can reduce pollution by CO and NOx.
- It can reduces the application of fossils fuel.
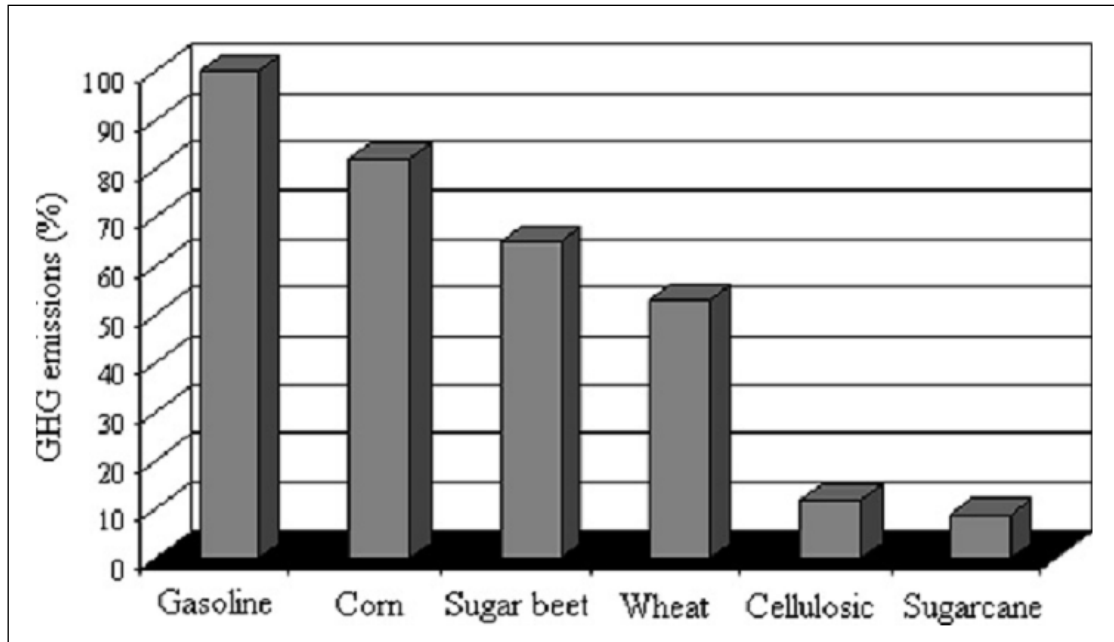
Fig18: Reduction of GHG Emission, Compared To Gasoline, Bioethanol Produced From Varity of Feedstock [48].

1.2.2 Type of BioEthanol Feedstocks:

Bio Ethanol can be produced from different types of raw materials. The raw materials have been classified into three category i)Agricultural Raw materials which include sugarcane ,sugar beet, fruits have full of sucrose ii)Starch materials (corn, Milo ,wheat ,rice ,barley etc) iii) lignocellulostic materials(wood, straw and grasses).Mainly now a day's corn, wheat, sugar corn and agricultural wastes are using for production of bioethanol. In Brazil mainly sugarcane use as bioethanol feedstock, wherein USA starch from corn, wheat use as raw material for bioethanol production. Among them mainly sugarcane is most popular feedstock and widely used for bioethanol production and sugarcane is mainly converted in to ethanol by fermentation process[49].

Table 3: Bioethanol yields from different energy crops [51]:

Country	Energy crops
Brazil	Sugarcane,100%
USA	Corn 98 %,Sweet sorghum, 2%
China	Corn 70%,Wheat 30%
Canada	Corn 70%,Wheat 30%
EU	Wheat 48%,Sugar beet 29%

There is another major problem related to biomass feedstock availability for bioethanol production. This availability can vary considerably from season to season and depends on geographic locations [50]. For this reason locally available feedstock will be used for bioethanol production. There are some reason for using of different biomass feedstocks for Bio Ethanol production as follows [51]:

- Chemical composition of the biomass.
- Cultivation Practices.
- Use of resources.
- contribution to biodiversity and landscape value losses
- Logistic cost (Transportation Cost, Storage of biomass)

The production cost of food crops are very much high. Which can highly effect on Bio Ethanol production. Because this type of feedstock has a high food value in socity [52]. Now for this reason there is a solution to overcome this problem by using lignocellulosic biomass for this purpose. Due to the increasing of food processing industry in various country can give huge resources of this type of biomass. This waste product has huge potential and can be used as alternative of fossils fuel. This type of materials can be classified into four type of biomass: (1) Forest Residues (2) Municipal Solid Waste (3)Waste Paper (4) Crop residues sources [56]. Lignocellulosic materials could produce up to 442 billion liters per year of bio ethanol [53]. Literature describes in several paper on various type of biomass such as rice straw [54], Corn Stover [55], etc.

1.2.3 Chemical structure and basic components of lignocellulosic materials:

Efficiency of bio ethanol production is varying with different feedstock of different composition.The structural and chemical composition of lignocellulosic materials is highly variable because of genetic and environmental influences and their interaction [56] Lignocellulosic materials consist mainly of cellulose, hemicellulose and lignin. This type of component mainly create about 90% of dry matter in lignocelluloses with the rest consisting of some minerals and ash [57].Mainly in lignocellulosic biomass cellulose forms the main skeleton which is associated by hemicellulose and lignin.
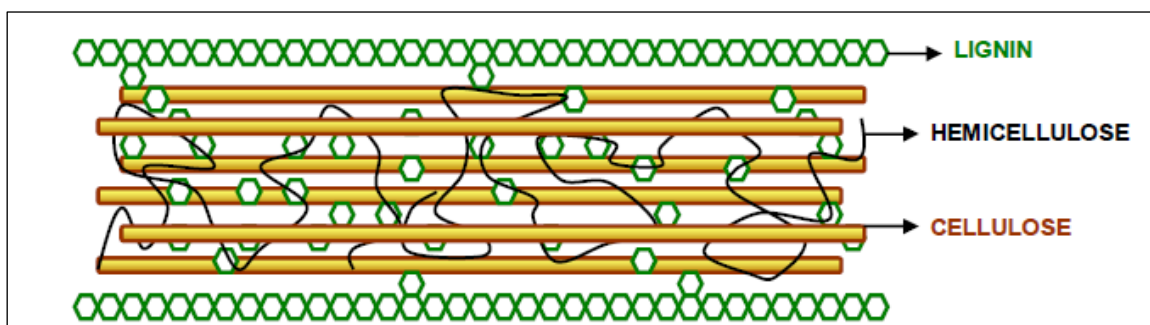
Fig 19: Representation of Lignocellulose Biomass Structure with three main component [58]

Figure 19 shows structural view of lignocellulosic biomass where lignin creates the main wall and protect hemicellulose and cellulose from any enzymes and acid attack. Cellulose is the major component of plant cell. It mainly provides strength and chemical stability. The Solar Energy is mainly stored into plant cell by photosynthesis process in the form of cellulose [**59**].Cellulose and hemicellulose is directly related to bioethanol production where lignin cannot be used in bioethanol production.

Cellulose is the major component (30%-60%) of total dry feedstock. It is mainly linear polymer of glucose. The orientation of linkage between the polymer chain and hydrogen bond create a rigid structure and difficult to break.In cellulose hydrolysis mainly this glucose polymer chain is converted in to free sugar molecules for further fermentation [**60**].This product sugar is mainly six carbon sugar.

Hemicellulose is another important component of lignocellulose biomass representing about 15%-25% of total dry matter. It can be extracted from the cell wall by alkali or acid solution. It is more easily hydrolyzed into monomeric sugar than cellulose. Hemicellulose contains xylose and arabinose (five-carbon sugars) and galactose, glucose, and mannose (six-carbon sugars) [**61**]. Highly content sugar in softwood is mainly mannose and in agriculture wastes is xylose .

Lignin is complex, high molecular weight, cross linked aromatic polymer which join cellulose and hemicelluloses compounds and construct lignocelluloses material. It also provides structural support and prevent lignocelluloses compounds from external stresses such as diseases insect [**62**]. Softwood generally contains more lignin than hardwood. Lignin in Lignocelluloses material creates many obstacle in fermentation process because lignin can prevent lignocelluloses biomass from any chemical degradation and biological degradation [**61**].

Ethanol can be also produced by reacting ethane with stream. But this process is not renewable. Mainly this process does not use renewable sources and release harmful gases in atmosphere. Energy require for production of ethanol from stream is very much high, So now a day's because of improvements in biotechnology, Bio ethanol produced from biomass has become a sustainable source of liquid fuels. In 2011, about 13.9 billion gallons of fuel ethanol was produced from corn starch in the United States [**63**].

1.2.4 Production of Bioethanol from lignocellulosic materials via biochemical process:

Bio ethanol production from lignocellulosic biomass through   scarification fermentation process is most popular process. There are several advantages of Bio ethanol production using fermentation method [**64**]:

- Mainly Renewable resources are used in fermentation process for Bioethanol Production.

- This process does not release harmful gases into atmosphere.

- We can start and stop the process any time in batch type fermentation production.

- Very little energy is required for this process.

- There is no requirement of high temperature and high pressure condition.

Now this efficient technology for bio ethanol production have also some disadvantages [**65**]

 (1) Internal structure of lignocellulosic biomass is more complex then starch. Because of complex polymer structure of cellulose, hemicellulose and lignin. The carbohydrate polymers are tightly bound to lignin mainly by hydrogen bonds but also by some covalent bonds. So for this reason delignification to liberate cellulose hemicellulose complex from lignin is very much important which become increased production cost.

(2) There are various type of sugar are released when hemicellulose and cellulose polymer are dissociated. So for this reason various genetically organism are required for efficient fermentation.

(3) Huge cost is required for storage of low density lignocellulosic materials.

(4) Due to using of various aqueous acid solution for enzymatic hydrolysis of cellulose to sugar destroy many simple sugar in the process

In spite of this following disadvantage this process has huge potentiality to produce low cost ethanol than starch based ethanol due to using low value of agricultural residues .

1.3 Fuel from biomass through fermentation Technology:

The basic process steps of bio ethanol production from lignocellulosic biomass are pre-treatment, hydrolysis, fermentation and product separation/distillation.

```
Biomass                                              Ethanol Product

  ↓
┌──────────┐    ┌──────────┐    ┌──────────┐    ┌──────────┐
│Pretreatment│→ │ Enzymatic│ →  │Fermentation│→ │  Ethanol │
│          │    │Hydrolysis of│  │          │    │ Recovery │
└──────────┘    └──────────┘    └──────────┘    └──────────┘
                    ↑                                 ↓
               ┌──────────┐                     ┌──────────┐
               │  Enzyme  │                     │  Solid   │
               │Production│                     │separation│
               └──────────┘                     └──────────┘
                                                      ↓
                                                ┌──────────┐
                                                │ Steam and│
                                                │  Power   │
                                                │Generation│
                                                └──────────┘
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                                                Ash to Disposal
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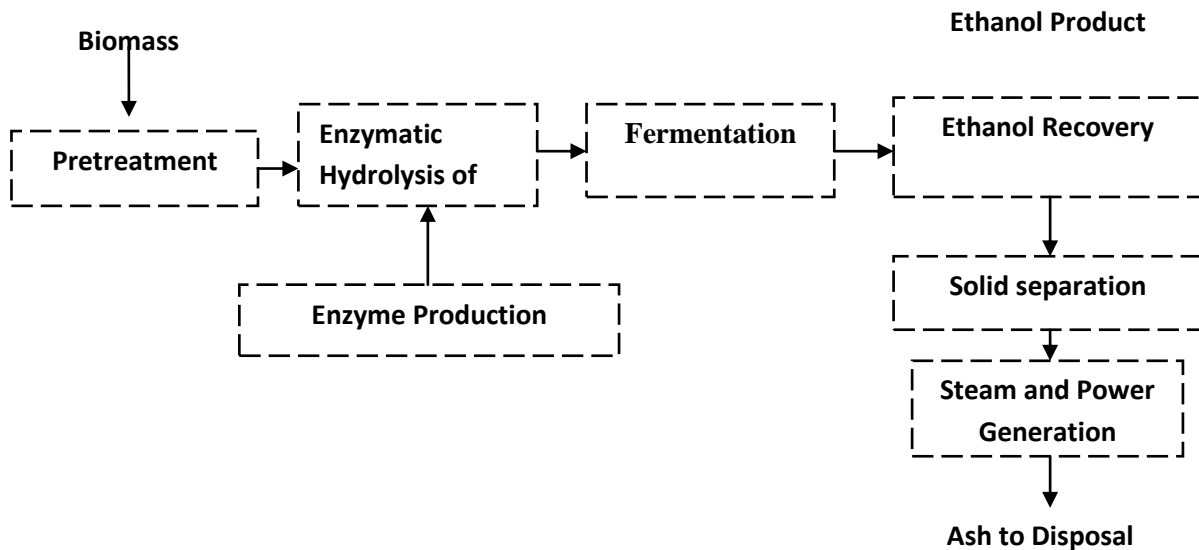
Fig 20: Thermo chemical /Biological Processes for Bio ethanol Production from Lignocellulosic Biomass [66].

1.3.1 Pre-treatment of lignocellulosic materials:

The roll of pre-treatment is very much important for bio ethanol production from lignocellulosic biomass. We get various benefits by using the pre-treatment process. This process is used to disrupt the chemical structure of biomass and increase the accessibility of enzymes to cellulose for better bio ethanol production. So the net fermentable sugar is increased due to this process. It improves the yield of bio ethanol production. Hydrolysis without preceding pre-treatment process yields typically less than 20% ethanol, whereas after pre-treatment the yield often exceeds 80% [67]. If the pre-treatment process is not completed successfully, the biomass is not easily hydrolysable by cellulose enzyme because of crystalline structure of the cellulose. So, the pretreatment process is very much important for the digestibility of lignocelluloses biomass.

For this reason the result is production of toxic compounds which will inhibit the fermentation process [68]. Pre-treatment can increase effective surface area of cellulose, improve the enzymatic digestibility of lignocellulosic biomass and reduce the overall cost for production by using cheap enzymes.

The cellulose and hemicellulose are cemented together by lignin. Delignification process is mainly used to remove this lignin and can improve the rate of enzymatic hydrolysis. This process is also a part of pre-treatment.

Hemicellulose is another important component in lignocellulosic biomass. It is a physical barrier which surrounds the cellulose fibres and can protect the cellulose from enzymatic attack. Many pre-treatment methods were shown to be able to remove hemicelluloses and consequently improve the enzymatic hydrolysis. But most of these processes partly remove the lignin as well, so the improvement is not the result of removal of hemicellulose alone [69]. Hemicellulose can be hydrolysed by hemicellulose hydrolysis. However, a suitable pre-treatment, like dilute-acid pre-treatment which removes the hemicellulose, eliminates or reduces the need for use of hemicellulose enzyme mixtures for degrading of biomass and produce xylose as a fermentable sugar [70].
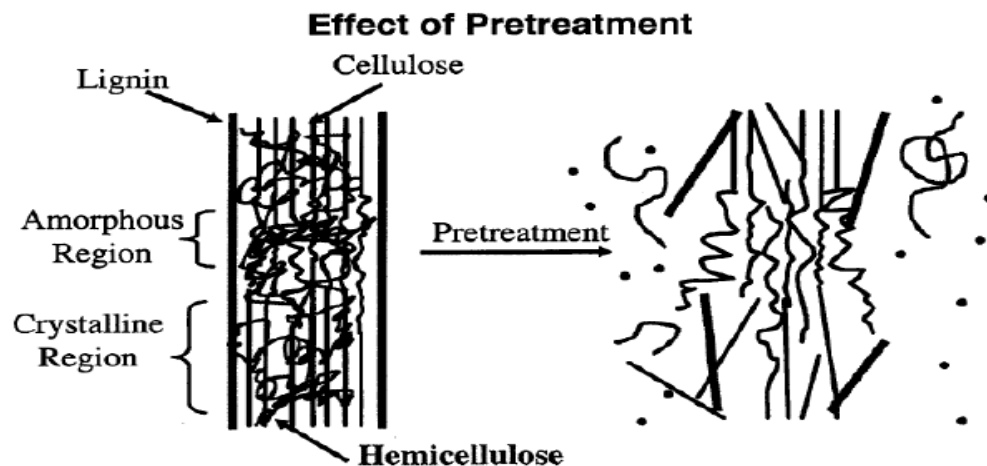
Fig 21: Disruption of Lignocellulosic Biomass by Pre-treatment Process [71]

Since the structures of lignocellulosic materials are very complicated their pre-treatment is not simple and totally depends on the type of materials. For pre-treatment of bark of poplar tree dilute acid pre-treatment is very much suitable but it is not effective for bark of corn [72].Physico-chemical (steam explosion/ auto-hydrolysis, hydro-thermolysis, and wet oxidation), chemical (alkali, dilute acid, oxidizing agents, and organic solvents), and biological processes have been used for pre-treatment of lignocellulosic materials.

In case of physical pre-treatment mechanical grinding is very much popular. Lignocellulosic materials can be broken by a combination of chipping, grinding, and milling to reduce cellulose

crystallinity. But Power Consumption is required very much high in this process than inherent biomass energy and there is a big chance of destruction of xylan portion of biomass [73].

In case of Physico-chemical pre-treatment steam Explosion is most commonly used method for pre-treatment of lignocellulosic biomass. This pre-treatment increases crystallinity of cellulose. Hemicellulose is easily hydrolyzed by steam explosion treatment. Steam Explosion also promotes delignification process. Generation of some compound during this process mainly produce obstacle in fermentation [74].

Ammonia fiber explosion (AFEX) is one of the alkaline physico-chemical pre-treatment processes. In this process, the material is subjected to liquid ammonia at high temperature and pressure, and a subsequent fast decompression, similar to the steam explosion, which causes a fast saccharification of the lignocellulosic material. Accessible surface area of cellulose is increased due to this process, it also removes lignin and hemicellulose. But this process is not suitable for high lignin content biomass [75].

Ozonolysis is a chemical pre-treatment process. It involves using ozone gas to break down the lignin and hemicellulose and increase the biodegradability of the cellulose. The pre-treatment is usually carried out at room temperature and is effective at lignin removal without the formation of toxic by-products. It has been widely used to reduce the lignin content of both agricultural and forestry wastes But it is very expensive process because large amount of ozone is required for removal of lignin [76]

In case of alkaline pre-treatment alkali solution is used to remove lignin and various uranic acid substitutions on hemicellulose because this type of compound mainly reduce accessibility of enzyme to the hemicellulose and cellulose. Sodium, potassium, calcium and ammonium hydroxide are appropriate chemicals for pre-treatment. NaOH is mainly used widely for this process. There is huge time required for completing of this process [77].

Acid pre-treatment is the most popular process in chemical pre-treatment category. It is mainly used for high yield of sugar from lignocellulosic biomass. Acid pre-treatment involves the use of sulfuric, nitric, or hydrochloric acids to remove hemicellulose components and expose cellulose for enzymatic digestion [78].This process can operate under high acid concentration and low temperature (concentrated acid pre-treatment) or low acid concentration and high temperature (Dilute acid pre-treatment) [63].While dilute acid pre-treatment are known to improve enzymatic hydrolysis and This pre-treatment method gives high reaction rates and significantly improves cellulose hydrolysis [79].Depending on the biomass between 80% and 95% of the hemicellulosic sugars can be recovered

by dilute acid pre-treatment from the lignocellulosic material [**80**].Which is used in fermentation process for production of bioethanol. Utilization of hemicellulose is very much important for economical use of biomass in bio ethanol production [**81**].So dilute sulfuric acid pre-treatment serves three important functions in the conversion process: [**82**] 1) Production of monomeric sugars from hemicellulose.2) exposure of cellulose for enzymatic digestion by removal of hemicellulose and part of the lignin.3) removal of inorganic compounds from biomass. In spite of these benefits this process also has some disadvantage [**83**]:1) Expensive material is mandatory in this process due to acid corrosion.2) acidic pre-hydrolyzates must be neutralized before the sugars proceed to fermentation.3) formation of degradation products and release of natural biomass fermentation inhibitors during this process.4) disposal of neutralization salts is needed.5) biomass particle size reduction is necessary.

There is another pre-treatment process called Biological pre-treatment which totally depend on microorganisms such as Brow-white- and Soft-rot fungi. That are mainly used to degrade lignin and solubilize hemicellulose. Lignin component of biomass is more affected then hemicellulose in case of biological pre-treatment. The advantage of Biological pre-treatment include low energy requirement however the rate of hydrolysis is very much low than other type of pre-treatment [**84**].

1.3.2 Enzymatic Hydrolysis:

Acid hydrolysis of lignocellulosic biomass has been known since 1819.This process is popular before use of enzymatic hydrolysis. Acid hydrolysis can be performed with several types of acids, including sulphurous, sulphuric, hydrochloric, hydrofluoric, phosphoric, nitric and formic acid. These acids may be either concentrated or diluted. There are mainly two types of acid hydrolysis process 1) Concentrated acid Hydrolysis 2) Dilute acid Hydrolysis [**85**]. Concentrated acid hydrolysis gives high yield of monomeric sugar. But using of large amount of acid can produce corrosion problem associated with equipment. Furthermore, when sulphuric acid is used the neutralisation process produces large amounts of gypsum which is one type of inhibiter for fermentation process [**86**].Now in case of dilute acid hydrolysis there is an advantage of low acid consumption relatively previous process. However high temperatures are required to achieve acceptable rates of conversion of cellulose to glucose and it also increase the rates of hemicellulose sugar decomposition and equipment corrosion [**87**].Due to this degradation product of hemicellulose can cause inhibition in the subsequent fermentation stage [**88**].Mainly acid hydrolysis is needed for conversion of biomass in to monomeric sugars in bioethanol production. However as mention earlier degradation product from cellulose and hemicellulose at high temperature may create some inhibition in fermentation step as well as lower yield of ethanol and sugars. So for this reason enzymatic hydrolysis of cellulose is used

instead of acid hydrolysis. This process have a potential of higher yield of sugars and reduce formation of toxic compounds than acid hydrolysis. Due to this process mainly dilute acid pre-treatment is very much important for expose the cellulose in to enzyme. This process can increases the digestibility of cellulose in the enzymatic hydrolysis step.

When hydrolysis is catalyzed by enzymes, the process is known as enzymatic hydrolysis. Conversion of 100% cellulose to glucose can be done in this process [89].Various species of fungi including Trichoderma, Penicillum and Aspergillus can produce this type of enzymes [90].The group of this type enzymes which are used to hydrolyze cellulose are called cellulase. The enzymatic hydrolysis process can be designed in various ways. The steps following pre-treatment hydrolysis and fermentation can be run as separate hydrolysis and fermentation (SHF) or as simultaneous saccharification and fermentation (SSF).The advantage of (SHF) is the ability to carry out each step under optimal condition. But major drawback of this process is sugars released inhibit the enzymes during hydrolysis. In SSF, the glucose produced is immediately consumed by the fermenting microorganism. But in this case ethanol can also act as an inhibitor in hydrolysis but not as strongly as glucose. In SSF due to the process integration that is hydrolysis and fermentation are performed in one reactor, can reduce number of reactors needed .So this process is very much cost effective. Utility cost of enzymatic hydrolysis is very much low compared to acid or alkaline hydrolysis because enzyme hydrolysis is usually conducted at mild conditions (pH 4.8) and temperature (318‑323 K) and does not have a corrosion problem [91].There are different factors that affect the enzymatic hydrolysis of cellulose, namely, substrates activity, reaction conditions (temperature, pH as well as other parameters), and a strong product inhibition. To improve the yield and rate of enzymatic hydrolysis, research has been focused on optimizing the hydrolysis process and enhancing the cellulase activity [84].The rate of enzymatic hydrolysis of cellulose is also dependent upon several structural features of the cellulose. Some common cellulose features which are known to affect the rate of hydrolysis include: (1) molecular structure of cellulose, (2) crystallinity of cellulose, (3) surface area of cellulose fiber (4) degree of polymerization (5) associated lignin or other materials[92].A low substrate concentration gives low yield and rate and a high cellulase dosagemay increase the processing cost of this step.

1.3.3 Fermentation:

The overall ethanol yield and the ethanol production rate depend not only on the sugar yield, but also on the ferment ability of the solution.

The solution of biomass now have both six-carbon (hexoses) and five-carbon (pentoses) sugars after enzymatic hydrolysis and pre-treatment process. Depending on the type lignocellulosic biomass the solution consists of glucose, xylose, arabinose, galactose, mannose, fucose, etc. We will get bio ethanol from this type of monomeric sugars. Mainly Microorganisms can be used to ferment all lignocellulosic- derived sugars to bio-ethanol.

The performance parameter of fermentation are: temperature range, pH range, alcohol tolerance growth rate, productivity, yield, inhibitor tolerance etc [93]. Yeasts like Saccharomyces cerevisiae and Zymomonas mobils have been mainly used for bioethanol fermentation [94].Thermophilic anaerobic bacteria like Thermoanaerobacter Ethanolicus have also been used as bio ethanol producer. The big advantage of thermophilic anaerobic bacteria over conventional yeasts is used variety of inexpensive biomass and their ability to withstand temperature extremes [95].

Fermentation process can be performed as a batch, fed-batch or continuous process. Mainly choice of most suitable process will be depend upon the kinetics properties of microorganisms and type of lignocellulosic biomass. Batch culture is mainly a closed culture system which contain mainly limited amount of nutrients and fermented by various microorganisms. It is very simple method after starting of this process nothing can be added except acid or alkali for pH control and air for aerobic fermentation.

Fed-batch process is mainly combination of batch and continuous process. It is widely used in industrial application. The major advantage of fed-batch, comparing to batch, is the ability to increase maximum viable cell concentration, allow product accumulation to a higher concentration.

In continuous process substrates, cultural medium, other require nutrients feed in to a vessel where the microorganisms are active. The product, which is taken from the top of the bioreactor, contains bio ethanol, cells, and residual sugar [52].

1.3.4 Ethanol Recovery:

As the biomass hydrolysis and fermentation technology is trying to develop continuously to increase the efficiency of bio ethanol production. Advancement in product recovery technologies will also be needed. This fermentation product is more volatile than water so for this reason distillation technology is good choice to separate ethanol from water in liquid mixture. The recovery of bio ethanol from distillation technology is about 99.6%. The solids from distillation are separated using a centrifuged and dried in a rotary dryer [51].

1.4 Literature Review:

1.4.1 Bio Ethanol Feed stock:

As the demand for clean energy is rising, research on renewable is being intensified as well. Bio ethanol is one of the most popular renewable liquid fuel. So for production of bio ethanol various types of raw materials are required. Several researchers have studied in different area of bioethanol feed stock like importance and types of biomass feedstock, reducing production cost by varying types of biomass feedstock, availability of different types of biomass depend on various parameters **[96,97,98,51]. Klass [96] and Lynd et al 1999 [97]** have worked on various types of bio ethanol feedstock and importance of biomass in production of bio fuel. Biomass is one of the most important resources for production of renewable energy on the earth. Biomass converts solar energy, carbon dioxide, and water into carbohydrates and oxygen by photosynthesis as follows:

$$nH2O + nCO2 + light \xrightarrow{\text{chlorophyll}} (CH2O) + O2.$$
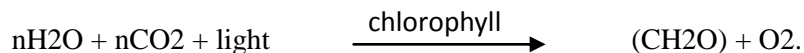
This equation have shown that plants capture around 0.1~1% of the incident solar energy. So huge quantity of biomass feedstock is required for bio fuel production. It also dramatically influence production cost, process development etc. Bio ethanol can be produced from different types of biomass feed stock like sugar, Starch based crops, lignocellulosic biomass. Starch-rich crops such as corn and wheat are commonly used for making bio ethanol commercially in the U.S But corn is mainly used as food crop and for this reason price of corn is more expensive than lignocellulosic biomass. Lignocellulostic biomass is popular bio ethanol feedstock due to its abundance and diversity like forestry and agricultural residue, municipal solid waste etc.But there is no clear idea about the processing method of bioethanol production from lignocellulosic biomass. **Sa´nchez and Cardona [98]** have analyzed how the production cost of bioethanol can be reduced by varying biomass feed stock (Cornstover, Cassava, Wheat, lignocellulosic biomass). In general, the use of sucrose-containing materials allows producing ethanol with the lowest costs compared to the starchy materials. On the other hand lignocellulosic biomass represents the most prospective feedstock for ethanol production. But there is no suitable comparison of production cost of bioethanol from various feed stocks. **Balat[51]** stated about the reason of variation in raw material and availability of bioethanol feedstock of various region in world. In this study the author stated various reasons like chemical composition, Cultivation Practices, availability of land, use of resources, absorption of minerals to water and soil etc. So there is no limitation of bioethanol feedstock around the world over the next decade.

1.4.2 Composition and structure of lignocellulosic biomass:

Lignocellulosic is one of the most abundant resources in the world. It is the most popular bio ethanol feedstock. Cellulosic ethanol processes mostly focus on solubilizing carbohydrates and converting the carbohydrates to ethanol with high yields, but cellulosic biomass has a complex structural of different compounds which is difficult to breakdown into sugars .So for this reason understanding of physical structure of lignocellulosic biomass is very much important. Many researchers are working on composition structure of lignocellulosic materials [**99,100,101,102,103,104].Chandra et al[99] and Kumar P et al[100]** have shown that the main component which compose plant cell walls are cellulose(35-50%),hemicellulose (15-35%), lignin (5-30%),and usually much smaller amount of pectin, protein, extractives, and ash. **Kulasinski et al [101]** have also stated about cellulose structure. The Lignocellulose is made of lignin and carbohydrates. Most important carbohydrate is cellulose. The plant cell is composed by micro fibrils that are formed by cellulose chain bound together by hydrogen bond. Cellulose is a polysaccharide that is made up of D-glucose bonded to each by b (1 $\longrightarrow$ 4) linkage forming linear chains. **Sun et al [102]** have also described the hemicelluloses structure which is another important component for bio ethanol production. Hemicellulose is a heterogeneous polymer and created short chains of polysaccharide molecules. They are composed of five different sugars monomers D-xylose, L-arabinose (pentoses), D-galactose, D-mannose and D -glucose (hexoses).They are usually found in the form of O-acety1-4-O methyl glucuronoxylans and O-acetylgalactoglucomannans depending upon the source of biomass. **Duval and Lawoko [103]** studied about the physical sructural of lignin. They have stated that lignin is the most abundant component in plant biomass. The three main lignin monomer that form the lignin polymer are phydroxyphenyl alcohol (H), coniferyl alcohol (G), and synapyl alcohol (S). **Ververis et al [104]** have shown that main obstacle is created by covalent bonding between lignin and cellulose during enzymatic hydrolysis. It has also been noted that woody biomass is harder to treat as compared to grass biomass because the extent of cross-linking and the phenyl content lignin found in wood is far more complex than that of grassy substrates.

1.4.3 Effects of Pre-treatment:

Ethanol produced from biomass has the potential to reduce conventional fossil fuel use and net carbon dioxide emissions. However, converting lignocellulosic biomass to ethanol is more difficult than corn, wheat, or sugarcane due to the complex structure of cellulose, hemicellulose, and lignin. So for this reason Pre-treatment is very much important step in bio-ethanol production. Many researchers are working on this process for improving efficiency of bio ethanol production. [**105,106,107,108,80**] **Mosier et al [105]** have analyzed the importance of pre-treatment process.

They have stated that this step is more costly step in bio-ethanol production. The goal of pre-treatment is to remove the lignin content from biomass, Hydrolyze hemicellulose to fermentable sugar monomers, Disrupt the complex structure of cellulose, hemicellulose, and lignin, and disturb the crystalline structure of cellulose to provide more available sites for enzymes. So this process can be reduced the production cost of bioethanol by reducing use of enzyme demand and producing high total glucose and xylose yields. **Taherzadeh and Karimi [106]** have studied diffrent pre-treatment technology such as Physical (milling and grinding), physico-chemical (steam explosion/autohydrolysis, hydrothermolysis, and wet oxidation), chemical (alkali, dilute acid, oxidizing agents, and organic solvents), and biological process. **Galbe and Zacchi [107]** have suggested that it is very much important to choose suitable pre-treatment process based on the lignocellulosic biomass properties of each raw materials, beacause different lignocellulosic materials have different physico-chemical characteristics .**Sun and Cheng [107]** have studied about dilute acid pre-treatment and stated that this process is suitable for biomass of high content hemicellulose. This process can be used for complete removal of hemicellulose and convert it in to monomeric sugar.high reaction rate, low acid consumption,and low cost of sulfuric acid are some of the advantages of dilute acid pretreatment. **Jeffries and Jin[80]** have stated that 80% and 95% of the hemicellulosic sugars can be recovered by dilute acid pre-treatment from the lignocellulosic material. So efficiency of bio ethanol production can be increase by using dilute acid pre-treatment.

1.4.4 Hemicellulose Hydrolysis:

The carbohydrate polymer in lignocellulosic need to be converted to simple sugars before fermentation through a process called hydrolysis .Hemi cellulose consists about 15% to 35% of plant tissue and contain valuable sugars which can be fermented to ethanol or other products. Several researchers are working on hemicellulose hydrolysis, propose various model for production of monomeric sugar from hemicellulose **[109,110,111,112,113,114].Yang and Wyman[109]** have shown that enzyme accessibility on cellulose can be increased by removing hemicellulose and result in higher glucose yields from cellulose. **Gamez et al [110]** have shown that hemicellulose can be converted in to xylose, mannose, acetic acid and galuctose. Among them xylose can be used for bioethanol production. **Saeman [111]** has developed a simplest kinetic model to describe hemicellulose hydrolysis. Which is based on two first order reaction. Where it is assumed that hemicelluloses are directly hydrolysed to xylose, which breaks down to degradation products in the second reaction. **Kobayashi and Sakai [112]** have shown another model of hemicellulose hydrolysis. Which is modified form of seaman model. According to this model it is assumed that there are two types of hemicelluloses, one fast reacting and one slow reacting.This modification was

based on the observation that the hydrolysis reaction rate decreases significantly after about 70% conversion. **Garrote G et al [113]** proposed another kinetic model of hemicellulose hydrolysis where oligomers play an important role. Oligomers are important intermediates during hemicellulose hydrolysis. According to this model it is assumed that there are two types of Oligomers, one long chain and another short chain. It is also assumed that short chain oligomers is directly converted into xylose and degradation products. **Kumar and Wyman [114]** have analysed that Yield of xylose from xylooligomers is increased with increasing acid concentration but decreased with increasing xylooligomer DP at a given acid concentration. So more acid is required for same xylose yield for higher DP spieces.

1.5 Scope of the Present Work:

In search of an alternative fuel due to the scarcity of fossils fuel, research on Bio ethanol production has taken a key role at present scenario. Biomass fermentation mainly generates Bio ethanol. Biomass is needed to convert into monomeric sugar for fermentation process. So for this reason Hydrolysis of hemicellulose and cellulose is needed for production of monomeric sugar. It is found that Enzymatic hydrolysis is the most effective process than acid hydrolysis. Because during acid hydrolysis yield of degradation product from cellulose and hemicellulose at high temperature may create some inhibition in fermentation step as well as lower yield of ethanol and sugars. So pre-treatment of biomass is very much needed before enzymatic hydrolysis .It is found that dilute acid pre-treatment is most effective one among others pre-treatment process for exposing cellulose into enzymes. This process has another advantage to convert total hemicellulose of biomass into monomeric sugar like xylose before enzymatic hydrolysis and can increase the yield of sugars for fermentation. The state of art reveals that although different work has been done on kinetic modelling of dilute acid pre-treatment of lignocellulosic biomass but the variation of percent yield of xylose, production of xylose at different acid concentration and different temperature of different biomass are yet to be researched. Therefore in the present work a study has been done for optimum production of xylose by varying acid concentration and temperature using different biomass. An computer programme is developed based on kinetic model of dilute acid pre-treatment. The effect of acid variation and temperature variation on xylose yield have been studied and net production of xylose have been computed for different biomass.

1.6 Objective of the Work :

- A computer programme is developed based on kinetic model of dilute acid pre-treatment.
- A study has been done for production of xylose from hemicellulose by applying model on different biomass.
- The effect of acid variation and temperature variation on xylose yield have been studied.
- Optimum production of xylose and optimum production time have been calculated for different biomass.

CHAPTER

2

Process Description

Mathematical Modeling

2.1 Process Description:

Ethanol Production from Biomass- Process Overview:
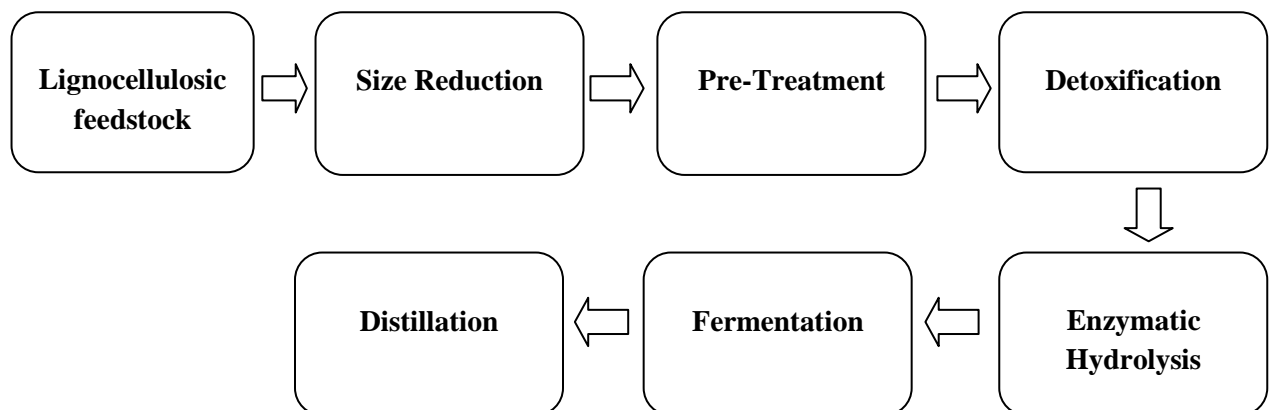
Fig22: General process for lignocellulosic based ethanol production [115]

There are three main types of feedstock commonly used for bio ethanol production- sugar-based, starch-based and lignocellulosic based. The conversion of sugar based feedstock to bioethanol is very simple as microorganism can use monomeric sugars to produce ethanol in a fermentation unit. During the conversion process of starch to ethanol a liquefaction step to make the starch soluble and a hydrolysis step to produce glucose are needed before the actual fermentation step **[115]**.The conversion process of lignocellulosic based feedstock to ethanol is more complex than starch-based and sugar-sugar based biomass. Size reduction and pre-treatment are required to change the structure

of biomass and increase the accessible surface area of cellulose, so that hydrolysis of carbohydrate fraction to monomeric sugars can be achieved more rapidly with better production. Detoxification is required to minimize the inhibitor compounds which may affect hydrolytic and fermentation steps. Enzymatic hydrolysis is needed to convert cellulose polymers to monomeric sugars using cellulose base enzymes. During fermentation process the monomeric sugars are converted to ethanol and ethanol is recovered usually by distillation.

In this study mainly two herbaceous (Cornstover & Switchgrass) and a woody (poplar) biomass are used as feedstock. Their compositions are as follows:

Table 4: Percent Dry weight composition of lignocellulosic feedstocks

Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Poplar [116]	49.9	22.4	18.1
Swichgrass [116]	31	20.4	17.6
Cornstover [117]	37.5	22.4	17.6

The yield of ethanol production from fermentation process totally depends on the efficiency of pre-treatment. The goals of ideal lignocellulosic pretreatment process are as follows [105]:

- Produce pentose in non-degraded form.
- Not lead to the release of compounds that significantly inhibit the fermentation.
- Require minimum size reduction
- Require minimum energy demand
- Process cost should be very much less.

From different pre-treatment techniques dilute acid hydrolysis is chosen due to the reasons described in section 1.2. In dilute acid pre-treatment sulfuric acid has been widely recognized as an inexpensive catalyst for hydrolysis of hemicellulose to sugars with high yields. Total hemicellulose hydrolysis of lignocellulosic biomass is completed during dilute acid pre-treatment which produces xylose. Unfortunately, conventional yeasts cannot ferment xylose to ethanol and the xylose is treated as costly waste disposal or burned as boiler fuel. But nowadays several yeast, fungi and bacteria have been discovered that can ferment xylose and produce ethanol. It can also decrease production cost of ethanol and percentage utilization of biomass is also increased [118].

In general hemicellulose hydrolysis models are based on acid-catalyzed breakdown of long chains of hemicellulose to form shorter oligomers that continues to break down to monomeric sugars. These monomeric sugars can be further degraded to furfural. Furfural itself has an inhibitory effect on the subsequent ethanol fermentation.

Process steps:

It is assumed that for modelling purpose acid pre-treatment can be divided into three sub-processes.

- Diffusion of water and acid inside the wood.
- Hydrolysis of hemicellulose sugars inside the woody particles.
- Diffusion of soluble sugars (reaction products) out of the woody particles.
- Mixing and bulk diffusion of soluble sugars in the pre-treatment unit.

Hemicellulose Hydrolysis:

The reactor configuration for hemicellulose hydrolysis, which is employed for acid hydrolysis, has been shown in Fig. 28:
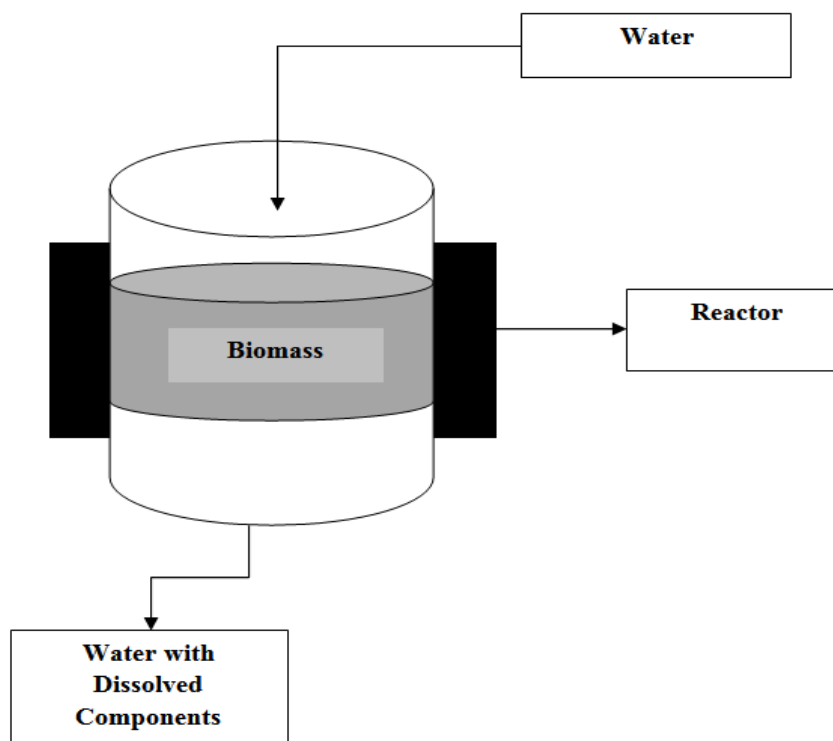

Fig 23: Flow-through reactor for acid pretreatment [115]

In this reactor hot water and acid enter from the top of the reactor and exit from the bottom containing the dissolved components. It is assumed that water can remain into the reactor for few minutes in our study. So for this reason concentration of sugars in bulk liquid phase would be very low and would not affect the diffusion of sugars from the surface of the wood to the bulk of water.

In this study biomass are pre-treated with acid concentration of (0.5, 1, 2 %v/v) at relatively high temperature of $140°C, 150°C, 160°C$ and hemicellulose of biomass is converted into primary xylose monomers and some soluble xylooligosaccharides with high yields.

2.2 Mathematical Modeling:

Mainly there are three types of models for hemicellulose hydrolysis. In the first model it is assumed that hemicellulose is directly hydrolysed to xylose, which breaks down to degradation products in the second reaction. The reaction mechanism is shown in Eq. (1) [115]:

$$\text{Hemicellulose} \xrightarrow{\text{K1}} \text{xylose} \xrightarrow{\text{K2}} \text{Degradation Products} \qquad (1)$$
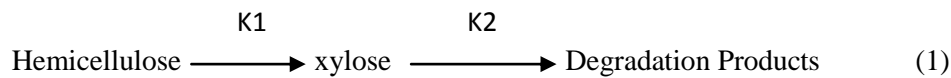
Second model is the modified version of first model. In the second mode, it is assumed that there are two types of hemicelluloses, one fast reacting and one slow reacting.This modification was based on the observation that the hydrolysis reaction rate decreases significantly after about 70% conversion.

The reaction mechanism is shown in Eq. (2) [115]:
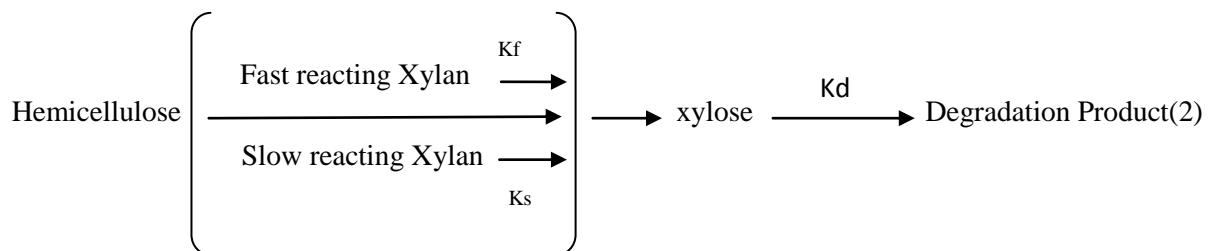
In case of second model it is also assumed that oligomers breakdown to monomers much more quickly than they are formed. For this reason in the second model oligomers stage have been omitted.

But in third variation of basic model, the oligomers step has been included. The reaction mechanism is shown in Eq.(3) [115]:

$$\text{Oligomers} \xrightarrow{K_1} \text{xylose} \xrightarrow{K_d} \text{Degradation Product (3)}$$
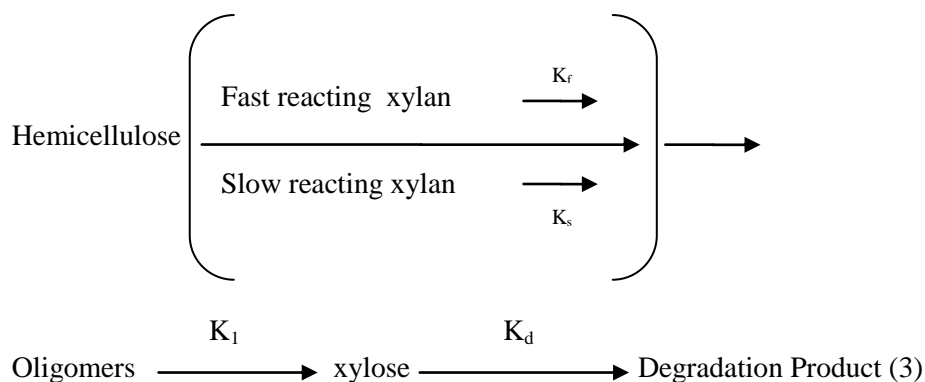
In this model it is assumed that reactivity of all oligomers is same and it is not a function of their size and molecular weight. As a result same reaction constant is employed for the disappearance of all

oligomers with different molecular lengths. But in our study it is assumed that reactivity of all oligomers are not same. According to this model hemicellulose of any biomass can be also divided into two parts based on degradation rate. One is fast hydrolyzing hemicellulose and another slow hydrolyzing hemicellulose. Fast and slow fraction of hemicellulose differ only slightly per substrate and are calculated to be about 65% and 35%, respectively, of most materials. So there are two degradation constants of hemicellulose of any biomass. But in our model it is assumed that total hemicellulose of any biomass is mainly fast hydrolysing type and has one degradation constant.

Single bond breakage for xylooligomers with DP ranging from 2 to 5 of all developed models has been based on breakage of bond at any time [114]. But in our study it is assumed that the probability of xylooligomer breakage from the middle of the chain is higher than the probability of the breakage from the side.

In our study a kinetic model of hemicellulose hydrolysis has been developed based on the above assumption with different xylooligomers ranging from two to five. Following a first order reaction, the reaction rate is:

$$\frac{d[X]}{dt} = -k[X] \tag{1}$$

Where, [X] is the concentration of the compound. Here mass fraction of compound has been considered to represent concentration, t is the hydrolysis time in min, and k is the rate of compound degradation in min^{-1}.

In our study following assumptions have been made:

- All degradation reactions follow first order kinetics.
- The reactions are irreversible.
- All xyloologomers have to de-polymerize to xylose before conversion to degradation products.
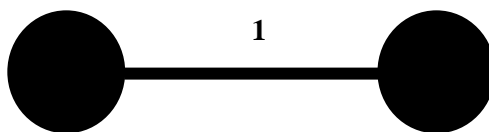
Xylobiose:

Fig 24: Moleculer structure of xylobiose [115].

There is only one bond in xylobiose and it has one possibility to hydrolyze and form two xylose molecules.

Xylose may break down to degradation products in the second reaction. In differential equation form this yield:

$$\frac{dC_2}{dt} = -K_2 C_2 \qquad (2)$$

$$\frac{dC_2}{dt} = 2K_2 C_2 - K_d C_X \qquad (3)$$

$$\frac{dC_2}{dt} = -K_d C_x \qquad (4)$$

Xylotriose:
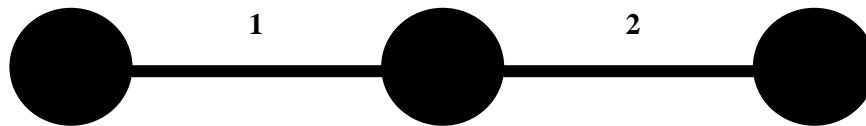
Fig 25: Moleculer Structure of xylotriose [115].

There are mainly two bonds in the xylotriose. Based on the assumption both have the same probability of breakage. When both bonds break at the same time, it results in three xylose molecule. Xylose may break down into degradation products in the subsequent reaction step:

$$\frac{dC_3}{dt} = -K_3 C_3 \qquad (5)$$

$$\frac{dC_2}{dt} = 0 \qquad (6)$$

$$\frac{dC_x}{dt} = 3K_3 C_3 - K_d C_x \qquad (7)$$

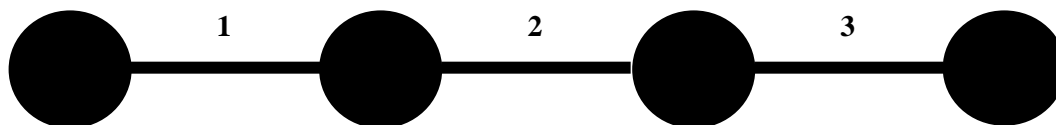$$\frac{dC_d}{dt} = K_d C_x \qquad (8)$$

Xylotetrose:

Fig 26: Moleculer Structure of xylotetrose [115].

There are three bonds in xylotetrose. Bond at position number one and three have similar position in the chain. So they have the same probability of breakage. Bond at position number two has a different position.

Here it is assumed that probability of breakage at bond two is α_4 and so probability of breakage of other twp bonds are (1-α_4). If bond at position two breaks the product will be two xylobiose molecule. If the bonds at position one and three break the product will be one xylobiose molecule and two xylose molecules. A simplified representation of this reaction scheme has been shown below:

$$\frac{dC_4}{dt} = -K_4 C_4 \tag{9}$$

$$\frac{dC_3}{dt} = 0 \tag{10}$$

$$\frac{dC_2}{dt} = 2\alpha_4 K_4 C_4 + (1-\alpha_4)K_4 C_4 - K_2 C_2 \tag{11}$$

$$\frac{dC_x}{dt} = 2(1 - \alpha_4)K_4 C_4 + 2K_2 C_2 - K_d C_X \tag{12}$$

$$\frac{dC_d}{dt} = -K_d C_X \tag{13}$$

Xylopentose:
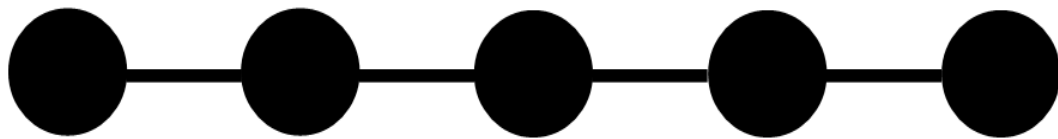
Fig 27: Moleculer Structure of xylopentose [115].

There are four bonds in xylopentose. Bonds at position one and four are at similar positions and bond position at two and three are similar. It is assumed that probability of breakage of bond in position two and three is α_5 and probability of breakage of bond in position one and four is (1-α_5). If bond at position two and three break the product will be two xylobiose molecules and one xylose molecule. If bond at position one and four break the product will be one xylotriose molecule and two xylose molecules.

A schematic representation of this reaction scheme has been shown below:

$$\frac{dC_5}{dt} = -K_5 C_5 \tag{14}$$

$$\frac{dC_4}{dt} = 0 \tag{15}$$

$$\frac{dC_3}{dt} = (1 - \alpha_5)K_5 C_5 - K_3 C_3 \tag{16}$$

$$\frac{dC_2}{dt} = 2\alpha_5 K_5 C_5 - K_2 C_2 \tag{17}$$

$$\frac{dC_x}{dt} = \alpha_5 K_5 C_5 + 2(1 - \alpha_5) K_5 C_5 + 3K_3 C_3 + 2K_2 C_2 - K_d C_x \tag{18}$$

$$\frac{dC_d}{dt} = -K_d C_x \tag{19}$$

Degradation Rate Constant:

The overall degradation reaction rate constants K_5, K_4, K_3, K_2, K_d, K_h have been computed by the Arrhenius equation. The Arrhenius equation for degradation rate constant is

$$K = k_0 [H^+]^m \exp(-E_a/RT) \tag{20}$$

Where K, k_0, H^+, m, E_a, R and T are the first order rate constant in min^{-1}, pre-exponential rate constant in min^{-1}, hydrogen ion concentration in mol/L, unit less acid concentration exponent, activation energy in kJ/mol, gas constant in kJ/mol-K and hydrolysis temperature in K respectively.

Table 5: Summary of Arrhenius Parameter for the degradation rate constant are as follows:

Compound	k_0 (min^{-1})	m (unitless)	E_a (kJ/mol/K)
Xylopentose [119]	2.71×10^7	0.302	55.94
Xylotetrose [119]	2.54×10^7	0.225	60.88
Xylotriose [119]	9.34×10^5	0.193	50.88
Xylobiose [119]	4.45×10^3	0.064	38.77
Xylose [120]	6.63×10^9	0.95	89.97

The difference of acid concentration exponent 'm' is small between xylopentose and xylotetrose. So it can be said that acid concentration is not a determining parameter for the depolymerization of xylopentose and xylotetrose. Activation energy of xylose is very high among other oligomers, .which also indicates that degradation rate constant of xylose strongly depends on temperature [119]. The disappearance rate of xylooligomers also increases with the length of the xylooligomers' molecular structure at all pH. It suggests that reaction step for oligomers with higher Degree of polymerization (DP) are much faster than lower DP.

Now K_h is the degradation rate constant of hemicellulose. The value of K_h depends on the type of biomass. According to our assumption, only the rate constant of fast reacting xylan is considered here. The value of reaction rate constant of hemicellulose is computed by using Arrhenius equation.

$$K_h = A. e^{E_a/(R.T)} \tag{21}$$

A= Pre-Exponential factor; E_a= Activation Energy (kJ/mol) ;R= 8.314×10^{-3} kJ/mol.K

The pre-exponentia factor, A is expressed as $(A_0 \times C_a^n)$ [118]

Therefore K_h= $A_0 \times C_a^n \times e^{-E_a/RT}$ (22)

Table 6: Kinetic Parameter of hemicellulose hydrolysis rate Constant (K_H) are as follows for different biomass [121]

Feedstock	A_0	n	E_a(kJ/mol)
Poplar [121]	3.3×10^{21}	0.4	176.7
Cornstover [121]	6.7×10^{16}	1.5	129.8
Swichgrass [121]	1.9×10^{21}	0.4	169

Diffusion Coefficient:

Another important parameter influencing the model prediction is the diffusion coefficient of species. In this model, mainly a wood particle is used as biomass for the hemicellulose hydrolysis. So during pre-treatment process mainly two diffusion process occur, one is the diffusion of water into the wood and other is the diffusion of soluble sugars out of the woody particle in aqueous solution. Driving force of diffusion is the concentration gradient of the diffusing species, which is either water or soluble sugars. One important factor for diffusion in a wood particle is the diffusion direction [115].It has been assumed that longitudinal diffusion exceeds diffusion in the radial and circumferential directions and therefore the transport process is considered as one-dimensional. It is mainly due to the cellular cavities that form obstacles for the water molecules in wood. Longitudinal diffusion is 10%-15% faster than radial and tangential diffusion [122]. For this reason it is assumed that radial and tangential diffusion is negligible compared to longitudinal diffusion in this model. In this study water absorption to the surface of the wood also has been neglected.

Now the gradient of water concentration is assumed to play an important part in the force responsible of the transport of water through wood. According to the Fick's first law water flow through wood is proportional to the concentration gradient.

$$J = -D \frac{\partial C}{\partial x}$$ (23)

Where J= flux of water, D = Diffusion coefficient, $\frac{\partial}{\partial x}$ is the gradient operator.

Now according to the Fick's second law $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x}\right)$ (24)

This equation can be used to express the transport of water by diffusion in the direction perpendicular to the surface of the woody particle [123].

During the pre-treatment two diffusion processes occur- one is the diffusion of water in the wood particle and the other is diffusion of soluble sugars out of the woody particle. In our study it is assumed that diffusion coefficient of all xylooligomers in water are equal.
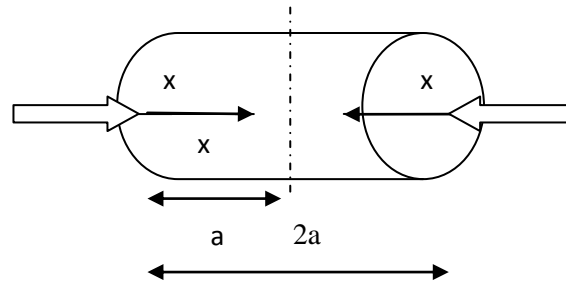

Fig 28: Simplified Representation of wood Particle [115].

Total length of wood particle =2a and regarding the initial and boundary condition of wood particle it is assumed that initial condition of water is zero inside the wood particle and surface concentration is one in this model.

The initial and boundary conditions are as follows:

At t=0, $0 < x < a$, C=0 (25)

At t=∞ , at x=0, C_w=1 & C=0 (26)

t=0, $0 < x < a$, C_H=0.25 (27)

Based on the above reaction constant value a model is developed. It is assumed that hemicellulose degrades to mixture of xylooligomers with xylooligomers ranging from one to five. A Flow Chart of the reaction mechanism is shown here:
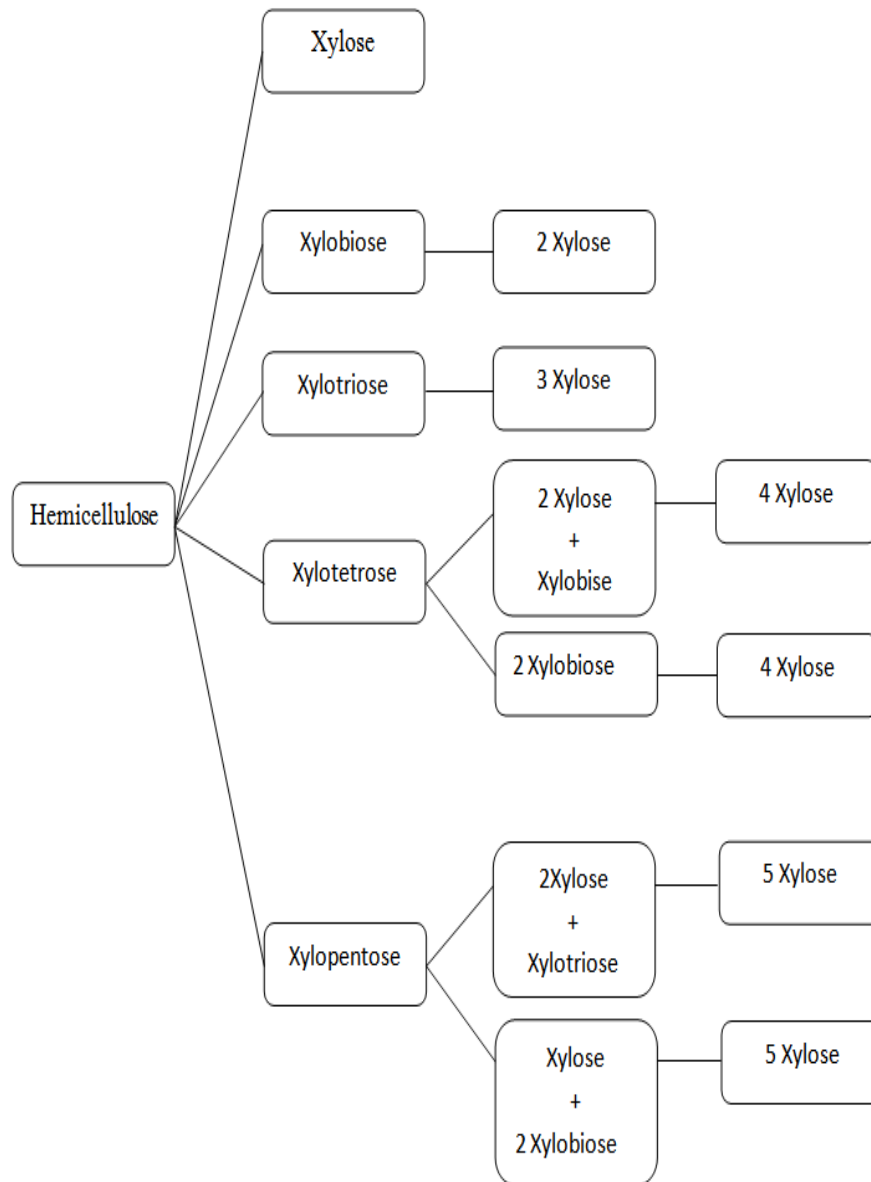
Fig 29: Mechanism of Hemi-cellulose Hydrolysis [115].

The following model equations are used in our study to simulate the total hemicellulose hydrolysis. The local concentration of water has taken into account in this model to show that the reaction starts when water molecules reach the hemicellulose. The xylose production rate from hemicellulose has been evaluated from the model. In addition the amount of total xylose production can be calculated from this model. In our process three types of biomass mainly Swichgrass , Poplar, Cornstover have been considered as the biomass feed. In our study kinetic model is totally based on

this acid treatment process. The concentration of water has taken in to account in this model equation to show that reaction starts when water molecule reaches the hemicellulose.

Model Equation:

Our kinetic model gives the concentration of each xylooligomer at any time and at any position inside the wood particle. The following equation are the kinetic model equation of our study:

$$\frac{dC_W}{dt} = \frac{d}{dx}\left(D\frac{dC_W}{dx}\right) \tag{28}$$

$$\frac{dC_H}{dt} = 0.2K_HC_HC_W \tag{29}$$

$$\frac{dC_5}{dt} = 0.2K_HC_HC_W - K_5C_5C_W + \frac{\partial}{\partial x}\left(D\frac{\partial C_5}{\partial x}\right) \tag{30}$$

$$\frac{dC_4}{dt} = 0.2K_HC_HC_W - K_4C_4C_W + \frac{\partial}{\partial x}\left(D\frac{\partial C_4}{\partial x}\right) \tag{31}$$

$$\frac{dC_3}{dt} = 0.2K_HC_HC_W + (1-\alpha_5)K_5C_5C_W - K_3C_3C_W + \frac{\partial}{\partial x}\left(D\frac{\partial C_3}{\partial x}\right) \tag{32}$$

$$\frac{dC_2}{dt} = 0.2K_HC_HC_W + 2\alpha_5K_5C_5C_W - 2\alpha_4K_4C_4C_W + (1-\alpha_4)K_4C_4C_W - K_2C_2C_W$$

$$+ \frac{\partial}{\partial x}\left(D\frac{\partial C_2}{\partial x}\right) \tag{33}$$

$$\frac{dC_X}{dt} = 0.2K_HC_HC_W + \alpha_5K_5C_5C_W + 2(1-\alpha_5)K_5C_5C_W + 2(1-\alpha_4)K_4C_4C_W + 3K_3C_3C_W +$$

$$2K_2C_2C_W - K_dC_XC_W + \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{34}$$

$$\frac{dC_d}{dt} = K_dC_XC_W + \frac{\partial}{\partial x}\left(D\frac{\partial C_d}{\partial x}\right) \tag{35}$$

Calculation of Xylose yield:

As mentioned earlier, the reaction starts immediately after water reaches the hemicellulose inside the wood particles. The xylose yield from wood particle can be defined by this equation:

Xylose yield per unit area per unit time $=1000 \times 60 \times D \times \left(\frac{dC_X}{dx}\right)$

Other xylooligomers yield can also be calculated by Eq. (35).

Where water density$=1000$ kg/m^3, $\frac{dC_X}{dx} =$ concentration gradient of xylose at the free surface of the wood particle.

Xylose yield (%) = (Xylose yield/ Total Yield)$\times 100 \tag{36}$

Total production of xylose from the wood particle can be calculated during hydrolysis by following equation:

Total Xylose Production = Xylose Yield$\times$ Area in longitudial Direction $\times (t_2 - t_1) \tag{37}$

CHAPTER

3

Results and Discussion

In this work a model of hemicellulose hydrolysis of lignocellulosic biomass mainly Switchgrass, Poplar, Cornstover have been analyzed for different temperature and acid concentration. Optimum acid concentration and temperature for maximum xylose yield of each biomass also have been studied here. A comparison of maximum xylose yield among the above-mentioned biomass has been shown here. The maximum xylose yield in percentage of Switchgrass for different acid concentration at 433 K are shown in **Figure 30.**
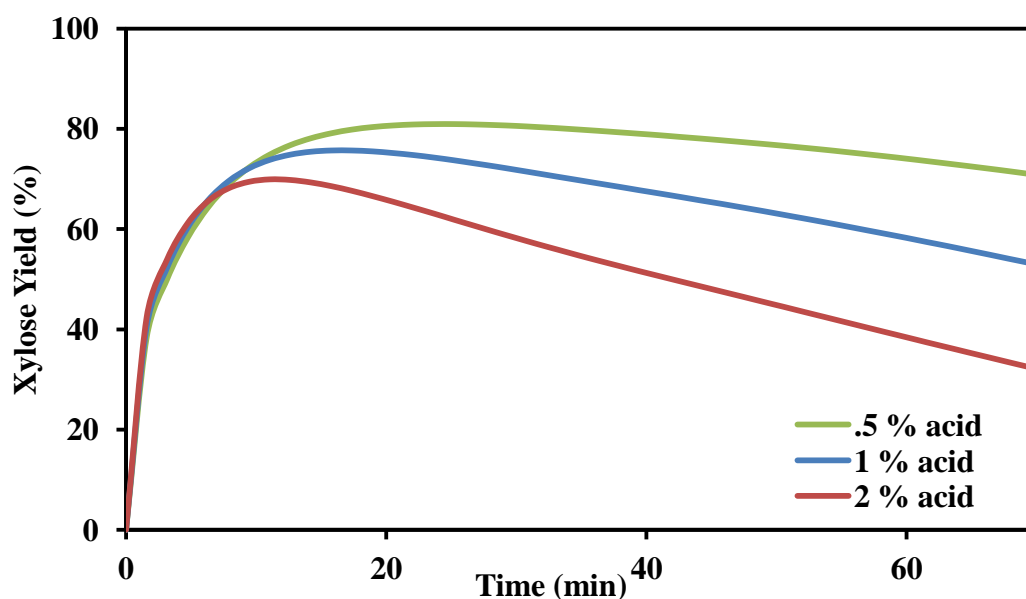

Fig 30: Variation of xylose yield with time at different acid concentrations for Swichgrass at 433 K

Three different acid concentration (0.5 v/v%, 1v/v%, 2 v/v %) of sulfuric acid at constant temperature of 433 K are used for xylose production. Swichgrass is used for hemicellulose hydrolysis. **Figure 30** shows percentage xylose yield of swichgrass at different time. Here we can clearly see that maximum xylose yield at 0.5% acid concentration is higher than other acid concentration. Maximum xylose yield of swichgrass at 0.5% of acid concentration is 80.94% of total solution of xylooligomers at 25 min. Where others maximum yield of xylose at different acid concentration are 76% for 1% acid concentration at 16 min and 70% for 2% acid concentration at 11 min. Value of degradation rate constant of xylooligomers must be decreased due to low acid concentration because degradation constant totally depend on the molarity of H+ of dilute acid solution. H+ molarity of solution can be varied by changing concentration of acid. So process time

for xylose production increase with decreasing acid concentration due to the low value of degradation rate constant of all oligomers. The trend of all these curves also represent that the slope of curve increase with increasing acid concentration at constant temperature, which indicates higher value of degradation rate constant of xylose. For this reason maximum yield of xylose can be increased with decreasing of acid concertation. So we will get more maximum yield of xylose at less than 0.5% acid concentration, but process time will be more, which is not efficient. But process time for 0.5% acid concentration is more efficient and profitable than 1% or 2% acid concentration. So optimum acid concentration for efficient production of maximum xylose yield should be at 0.5%.
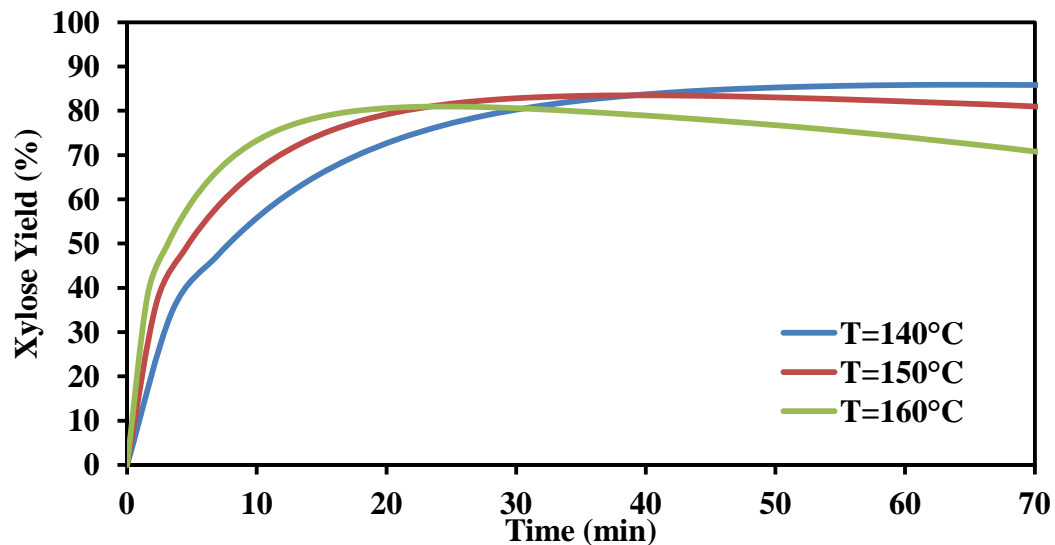

Fig 31: Variation of xylose yield with time at different temperature for Swichgrass at 0.5% acid concentration

Three different Temperature (140℃, 150℃ ,160℃) at constant acid concentration of 0.5% are used for xylose production. **Figure 31** shows percentage xylose yield of swichgrass at different temparature for different time. Here we can clearly see that maximum percentage xylose yield is 86% of total solution of xylooligomers at 66min for T=140℃. Where others maximum yield of xylose at different temperature are 83% at 41 min for 150℃ and 80.94 % at 25min for160℃. Among all of them production of xylose at T=140℃, 0.5% acid concentration is very much profitable but most efficient process is at T= 150℃. The trend of the curve also represents that by increasing temperature total process time decreases sharply. By increasing temperature can increase the degradation rate of all oligomers, as well as xylose. So for production of maximum yield of xylose at higher temperature is not suitable. By analysing all values of percent xylose yield at different temperature a conclusion has been taken that optimise temperature for efficient production of maximum xylose yield should be taken at T=150℃. Because at T=150℃ requirement of time is very

much less than other temperature. However T=140℃ can be produced higher percentage of xylose, but we can minimize this different of maximum yield by repeating process again atT = 150℃. So optimize conditions for maximum xylose yield of swichgrass are **0.5%** acid concentration and **T=150℃.**

The maximum xylose yield in percentage of Poplar for different acid concentration at 433 K are shown in **Figure 32.** Three different acid concentration (0.5 v/v%, 1v/v%, 2 v/v %) of sulfuric acid at constant temperature of 433 K are used for xylose production. We can clearly see that the trend of all curves for both poplar and swichgrass are same because of the same internal structure. It is evident from the figure that maximum xylose yield at 0.5% acid concentration is higher than other acid concentrations. In case of 0.5% acid concentration, the maximum yield of poplar is 80.85% at 25.25 min. whereas the other maximum yields of xylose are 69.7% for 2 % acid concentration at 12 min and 75.5 % for 1% acid concentration at 17 min. However trends of all the curves indicate that degradation of xylose at 0.5% is less than other acid concentrations. Because degradation constant totally depends on the molarity of H+ of dilute acid solution and can be varied by changing concentration of acid. By analysing all values of percent xylose yield at different acid concentration a decision has been taken that optimum acid concentration for efficient production of xylose of poplar should be 0.5%.
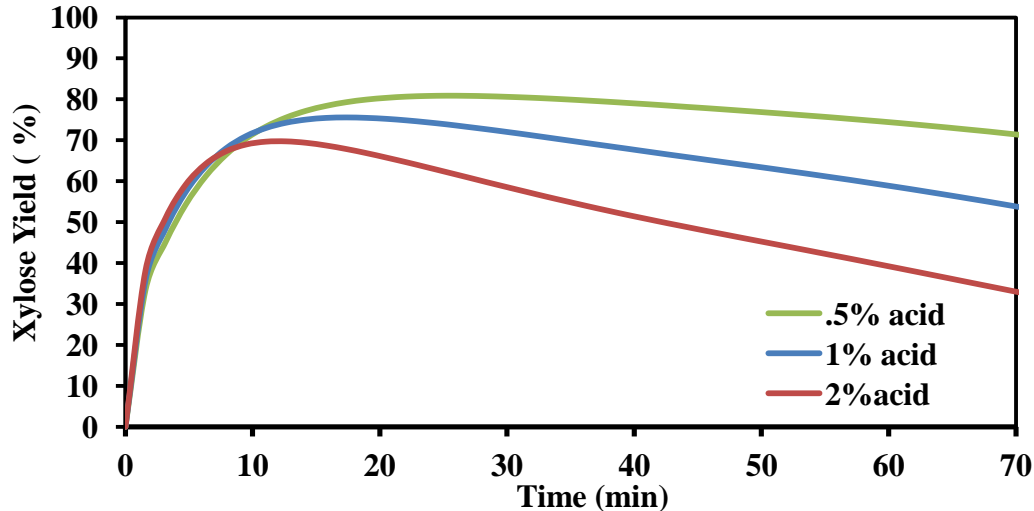
Fig 32: variation of xylose yield with time at different acid concentration for poplar at 433K temperature

Figure 33 shows three different temperatures, viz. (140℃, 150℃ ,160℃), at constant acid concentration of 0.5% for percent xylose production in poplar. We get different percentages of the maximum xylose yield at different temperatures, but after getting all these values we can say that the production of xylose at T=160℃ is very much profitable for poplar biomass.

Fig 33: Variation of xylose yield with time at different operating temperatures for Poplar at 0.5 v/v% acid concentration

Due to the high degradation constant value at higher temperature, the maximum production of xylose will be automatically decreased. So higher value of temperature is not always efficient in case of xylose production. By analyzing all the values, it is evident from this graph that the maximum percentage xylose yield of poplar should be 160℃.

Now there is another graph for analysing percentage yield of cornstover for different acid concentration at a constant temperature of 413K are shown in **Figure 34**. Three different acid concentration (0.5 v/v%, 1 v/v%, 2 v/v %) of sulfuric acid at constant temperature of 413K are used for xylose production. We can clearly see that the maximum xylose at 0.5% is higher than other acid concentrations. Where other maximum yield of xylose at different acid concentration are 81% for 1% acid concentration at 42min and 76% for 2% acid concentration at 32 min. Mainly from this result we can say that value of degradation constant totally depend on the molarity of H+. Molarity of H+ is related to the acid concentration of a solution. So the reaction constant can be varied by using different acid concentrations. There is an advantage of using low value of degradation constant because it can help to increase maximum xylose yield of hemicellulose hydrolysis. But process time may be increased due to the use of low value of degradation constant because process time is totally dependent on the degradation constant rate of xylooligomers.

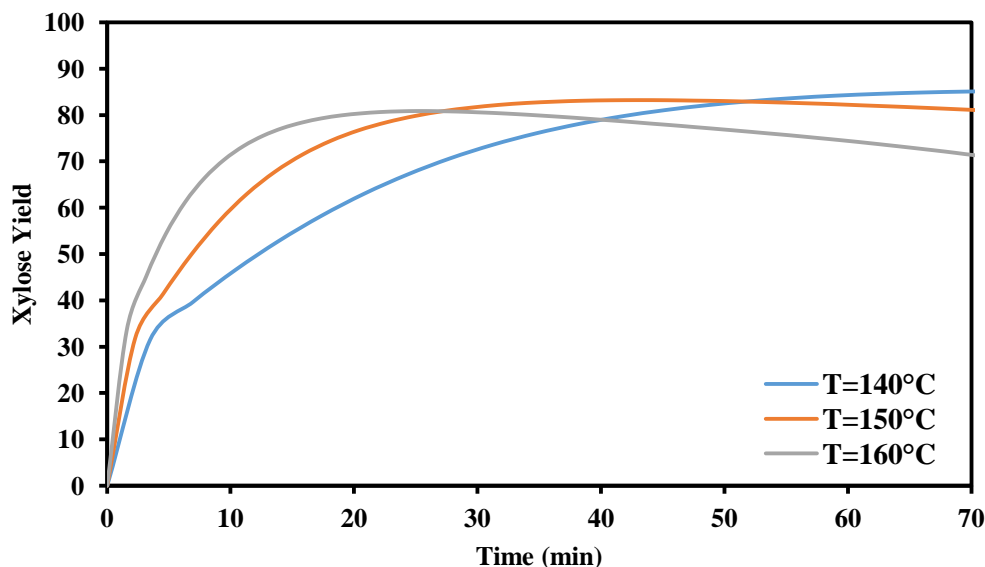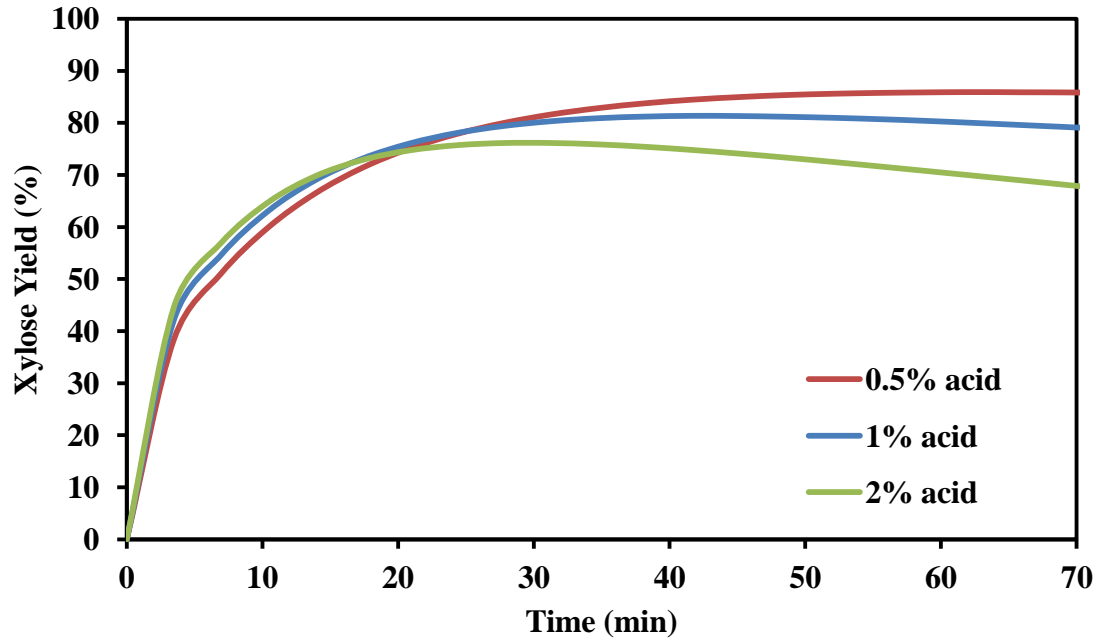**Fig 34: Variation of xylose yield with time at different acid concentration for Cornstover at 413K**

So by analysing all value of xylose yield of cornstover a decision has been taken that maximum xylose yield of cornstover will be in range of 76% -86% depend on acid concentration, but according to our study optimum value of acid concentration should be 0.5% for efficient production.

Figure 35 shows variation of percentage xylose yield cornstover with variation of temperature. Three different temperature of $(140℃, 150℃, 160℃)$ at constant acid concentration of 0.5% have been used for xylose production. Here we can clearly see that maximum xylose yield is 86% at $T = 140℃$ and lowest production of xylose of 81% at $T=160℃$ .But the most profitable and efficient temperature for maximum yield of xylose should be$150℃$. The trend of all curves also represent that by increasing temperature total process time decrease sharply. However we can increase the degradation rate of all oligomers as well as increasing degradation rate constant of xylose by increasing temparature. So for production of maximum yield of xylose at higher temperature is not suitable. So a decision has been taken by analysing this graph that optimum temperature should be 150℃ at 0.5% acid concentration.
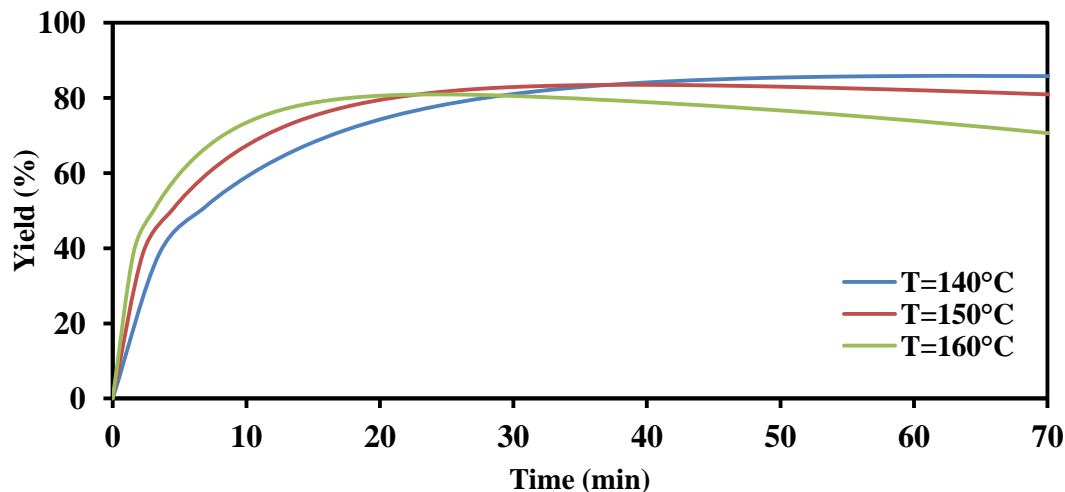
Fig 35: Variation of xylose yield with time at different operating temperatures for cornstover at 0.5 v/v% acid concentration

After analysing maximum xylose yield of above three types of biomass at different acid concentration and different temperature we can clearly see that production of xylose from swichgrass is maximum among other biomass at **0.5%** acid concentration and **160℃**.

Now the percentage yield of xylooligomers of swichgrass at optimum condition of 0.5% acid concentration and 160℃ has been shown in **Figure 36.**

Fig 36: Yield Percentage of various xylooligomers of swichgrass

Figure 36 shows the variation of yield percentage of xylooligomers of swichgrass at 0.5% acid concentration and 160℃. It has been observed that the degradation rate of Xylopentose, Xylotriose are very much higher than Xylose. We can see that production of furfural will be increased sharply with the increase in process time.

CHAPTER

4

Conclusion and Scope of Future Work

4.1 Conclusion:

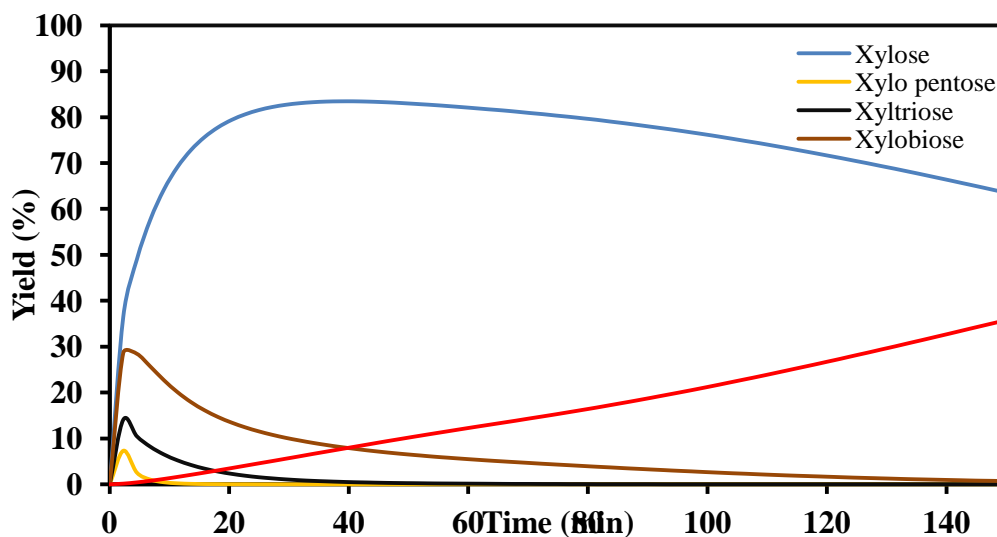A study on hemicellulose hydrolysis for production of xylose has been analysed and a comparison of xylose production of different biomass have been studied in this thesis. After applying kinetic model on three different biomass (Swichgrass, Poplar and Cornstover) for production of xylose a conclusion has been taken that production of xylose from Swichgrass is maximum among all of them . Optimum Condition of maximum yield of xylose for Swichgrass are 0.5% concentration of sulfuric acid with temperature of 150℃. The following conclusion can be drawn from the study. The total numerical design is done in Dev-C++.

Dilute acid pre-treatment is an efficient process for hemicellulose hydrolysis and xylose production.

1. The model computes the concentration of xylose, other xylooligomers and water inside the biomass as an unsteady solution.
2. The yield of xylose from the end face of the biomass pellet is computed using the concentration distribution.
3. With the increase in acid concentration degradation constant of xylose increase indicating the decrease in maximum yield of xylose.
4. Higher process temperature can increase the degradation constant of xylooligomers and reduce to total process time, but due to higher process temperature maximum xylose yield may be reduced.
5. Among the all three biomass efficient feedstock for xylose production will be Swichgrass.

4.2 Scope of Future Work

- The present work is done on xylose production from hemicellulose hydrolysis. The work may be extended further with addition of another modelling of ethanol formation from xylose.
- Maximum production of xylose from this model can be done by using other type of biomass.

- This present work is done on xylose production from hemicellulose having single degradation constant. But the work may be extended further from hemicellulose having two degradation constant.

- This study may be extended also for multidimensional transport of dilute acid solution in a wood chip.

- This present work is done on the reactivity of xylooliogomers with degree of polymerization (DP) ranging from 2 to 5. This work may be extended further by increasing this range of xylooligomers for more conversion of hemicellulose in to xylose.

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