Study of thermo-chemical kinetics of raw and pre-treated industrial lingocellulosic waste biomass and coal blends during pyrolysis

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DEDICATION

Traveler, there is no path,

the path must be forged as you walk.

Antonio Machado

Dedicated to my father,

who always supported me, whatever path I took.

ACKNOWLEDGEMENTS

ABSTRACT

Coal co-pyrolysis with sustainable power source, for example, biomass like wood squander, rice husk and wheat straw etc. could be used as an elective path for energy generation. High-quality fuel production using low position coal and biomass is imperative from the perspective of sustainable power source and the usage of unused assets. Towards this objective, pretreatment could be assumed a good job in upgrading physiochemical properties of biomass. Organosolv pretreatment, being a novel technique, improved the cellulosic content of lignocellulosic biomass by expelling the lignin content and adjusting the physical structure of biomass. In this work, organo-aqueous pre-treatment of industrial lignocellulosic rice husk RH at 80˚C and for 3 hours using glycerol. Glycerol-water percent content is used as process variable (100% Glycerol G, 75% G, 50% G, 25% G). Pre-treated industrial lignocellulosic RH is then mixed with low position coal C of Pakistan origin in a weight ratio of 50:50. Samples are subjected to proximate, ultimate, chemical and structural analysis to study the impact of glycerol pretreatment. In addition, thermogravimetric analysis (TGA) is performed under inert environment at various heating rate (10, 30, 40˚C) to the temperature range from 30-900˚C was carried out. Carbon, hydrogen and cellulose content is improved after treating biomass with glycerol solutions. Apparently, the thermal profile of coal and pre-treated lignocellulosic biomass blends appear to correlate with percentage of Glycerol added for the pretreatment of RH. Also, first order reaction model Flynn Wall Ozawa F-W-O method was used to determine the kinetic parameters and activation energy for the coal and pretreated biomass blend. The highest value of activation energy that is 198.51 kJ/mol is obtained in the case of coal-rice husk blend having RH treated with 75% solution of glycerol. Fuel creation from biomass and coal could be an option and more practical approach to proficiently use coal and biomass together for power and vitality generation.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

EU	European union
UN	United Nations
FWO	Flynn Wall Ozawa technique
RH	Rice husk
C	Coal
G	Glycerol
V.M	Volatile matter
M.C	Moisture content
TGA	Thermogravimetric analyzer
FTIR	Fourier transform infrared spectroscopy
GCV	Gross calorific value
R1	Rice husk treated with 100% sol. of Glycerol
R2	Rice husk treated with 75% sol. of Glycerol
R3	Rice husk treated with 50% sol. of Glycerol
R4	Rice husk treated with 25% sol. of Glycerol
RC	Coal-biomass blend having un-treated biomass
RC1	Coal-biomass blend having treated biomass with 100% Glycerol sol.
RC2	Coal-biomass blend having treated biomass with 75% Glycerol sol
RC3	Coal-biomass blend having treated biomass with 50% Glycerol sol
RC4	Coal-biomass blend having treated biomass with 25% Glycerol sol

Chapter 1

Introduction

1. Introduction

(Basic Introduction of industrial cellulosic bimaoss, coal, coal biomass blends and its potential applications are elaborated in this chapter. It includes problem statement and objectives of this study. It concluded with thesis outline.)

1.1 Basic Introduction

Because of consumption in petroleum derivatives holds, increment in their value, greenhouse impact and natural contamination, world present challenge is to lessen its reliance on non-renewable energy source by creating manageable and sustainable power source supply [1].

Biomass is utilized for getting vitality by consuming wood, and other natural organic material. Consuming biomass discharges carbon emanations, yet has been classed as a sustainable power source in the EU and UN lawful systems, since plant stocks can be supplanted with development and growth of new plants. It has turned out to be mainstream among coal control stations, which change from coal to biomass so as to change over to sustainable power source, without squandering existing power generating plant and framework. Biomass frequently alludes to plants or plant-based materials that are not utilized for feeding purpose, and are explicitly known as lignocellulosic biomass. As a vitality source, biomass can be utilized specifically through ignition to deliver heat, or by implication in the wake of changing over it to different types of biofuel. Change of biomass to biofuel can be accomplished by various techniques, which are extensively arranged into chemical, thermal, biochemical etc.

The issue of ozone depleting gases discharge and limited stock of non-renewable energy sources has been pushing a move far from the utilization of non-renewable energy sources for vitality production. Burning of non-renewable energy sources is a noteworthy supporter of carbon dioxide CO_2 emanations, connected to a worldwide increase in temperature and causing the environmental change. The non-sustainable nature of these energy getting fuels implies that their stores would be reduced soon, by certain projections, coal reserves would diminished inside a century [2].

The worldwide utilization of coal has developed quickly and will most likely to be increase in near future. A few analysts recommended that co-pyrolysis or co-combustion of coal and sustainable power source, for example, biomass like rice husk, wheat straw, wood squander, etc. could be used as an elective course for energy production, especially in retrofitting boilers already installed [3]. Co-pyrolysis or co-combustion of biomass and coal mixes can lessen NOx and SOx levels in exhaust gases [4].
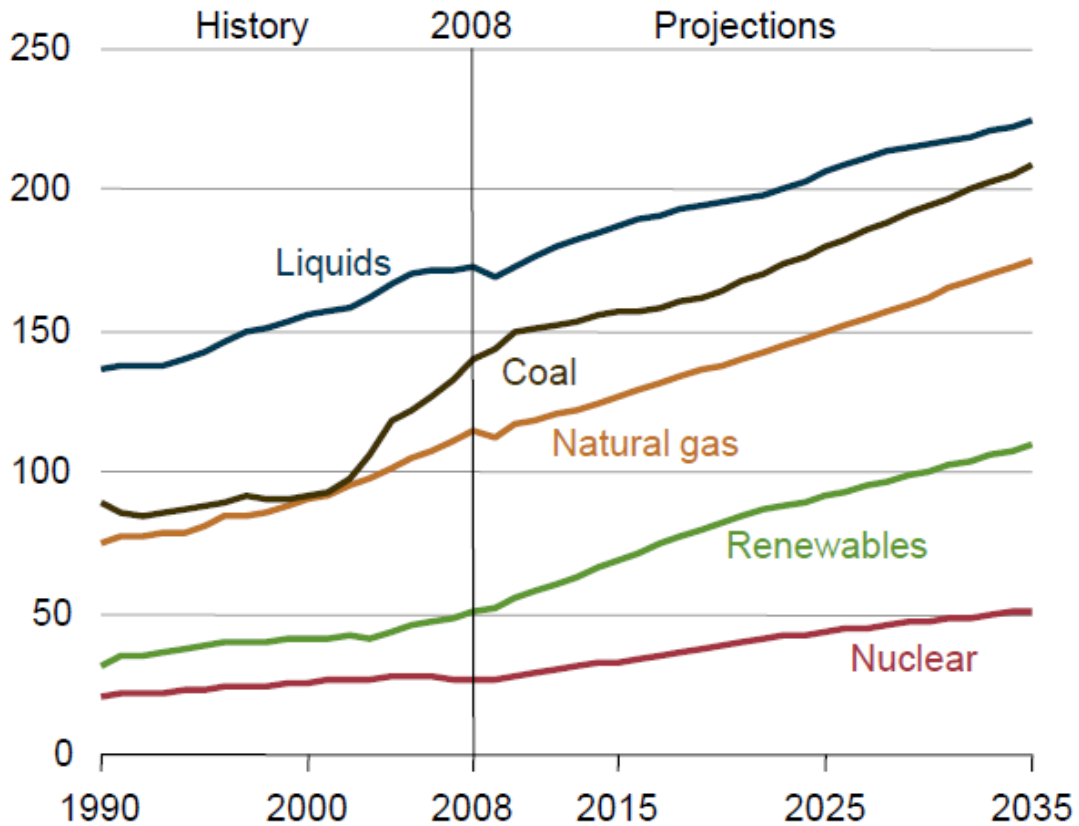
Figure 1-1: World energy consumption by fuel, 1990-2035 (quadrillion BTU) Source: U.S. Energy Information Administration.

Along these lines, Biomass is turning into an inexorably imperative supporter of the worldwide energy mix, because of being both generally neutral in carbon over its life cycle and also renewable and sustainable, whenever developed reasonably. Biomass co-pyrolysis or co-combustion with coal is being perceived as an especially appealing suggestion for energy production since it gives a quick and handy methods for decreasing coal utilization. Biomass co-pyrolysis or co-combustion is perceived as a significant innovation to help in

controling the utilization of petroleum products, especially because of its general simplicity of usage [1].

Biomass is an inexhaustible asset whose utilization for vitality is friendlier to nature than the utilization of coal or any other petroleum derivative. Fuel creation from biomass and coal could be an option and more practical approach to proficiently use coal and biomass together for power and vitality generation. On the off chance that biomass is developed as well as utilized sustainably and economically, it is more neutral of CO_2, and also its price will not much fluctuate with passage of time. This implies it can possibly be a practical and economical supply of vitality. Biomass is the main sustainable resource of fixed carbon and is viewed as the sustainable power source with the best potential to add to the vitality needs of present day society. The most imperative ecological motivation to consider a move toward bioenergy is worries about a worldwide temperature alteration, since non-renewable energy source use adds to environmental carbon, and certain petroleum product inventories are nearly getting to be drained. On the off chance that biomass is utilized with coal to generate energy, the ecological effect of petroleum product use could be decreased and the carbon impression will be diminished [5].

The expression "lignocellulosic biomass" is utilized when alluding to softwood, higher plants, or hardwood. The principle segments of the lignocellulosic materials are cellulose, lignin and hemicellulose [6]. Diverse kinds of biomass, for example, herbaceous plants, woody plants, grasses, amphibian plants, agrarian harvests and deposits, etc. contain distinctive quantity of lignin, cellulose, hemicellulose, and extractives [7].
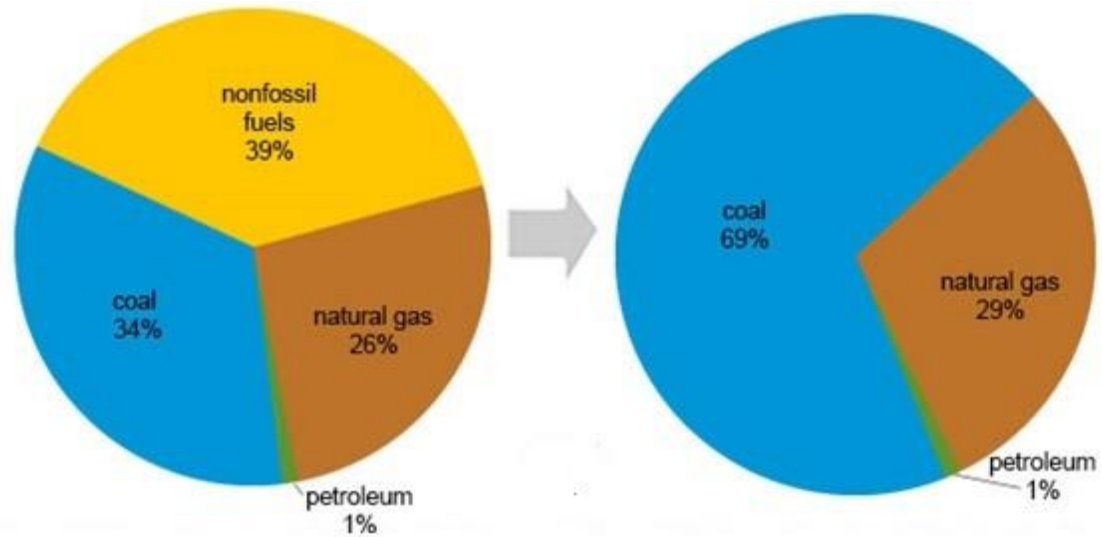
Figure 1-2: Major Energy/fuel resources used for power generation and resulting CO_2 emission from electric power sector by fuel type. Source: US energy information administration.

Aside from the three fundamental synthetic compounds which lignocellulose comprises of, complex also contains water in it. Moreover, minor quantity of minerals, protein and different other constituents are also present in the lignocellulose structure [5].

1.2 Problem Statement

Biomass may have ideal fuel qualities, for example, low quantity of Sulphur, low ash content etc. However, It also have some disadvantages like high content of water, low calorific esteem etc. Then again, as of now, the fundamental worldwide exchange of coal is with high position coal, which is up just 50% of entire coal stores. That is why, it is estimated that the supply of the coal will move to low position coal in coming decades. Low position coals for the most part have low calorific esteem, high content of water, higher sulphur content, high ash content etc. Therefore, transformation of both low position coal and biomass to fantastic fuel is imperative from the perspective of usage of low quality or low postion coal with biomass more efficiently and to decrease emission of carbon dioxide in environment [8].

That is why, we need to create or develop some pre-treatment procedures, so as to improve the quality of both coal as well as biomass material.

1.3 Research Objectives

Typical sub-bituminous coal and industrial lignocellulosic biomass residues rice husk, is used as raw material. The main objectives are:

- ➢ Pre-treatment of biomass to improve the quality of biomass.
- ➢ Co- pyrolysis of coal, un-treated and treated biomass.
- ➢ Investigation on thermo-chemical behavior of un-treated and treated biomass and coal blends.
- ➢ Kinetic study on co- pyrolysis of coal, un-treated and treated biomass.

1.4 Thesis Outline

In Chapter 2, the relevant theoretical background and literature review related to pretreatment of biomass and co-pyrolysis of coal biomass blends is given. In short, literature review describes potential of energy production for coal biomass blends, reduction in green house emissions, effects of various pretreatment on physio chemical properties of different biomasses especially glycerol organo-solvent effect on rice husk.

Materials and methodology that is followed in this study is outlined in chapter 3. Rice husk and glycerol are the materials that are used. Experimental methodology used for the pre-treatment of biomass is also described. Moreover, theoretical background of characterization techniques (Thermogravimetric analyzer, ultimate analysis, Fourier transform infrared spectroscopy, bomb calorimeter) are also explained in this chapter.

In Chapter 4, results after characterization are presented here and discussion is carried out. In particular, results of thermogravimetric analysis are described and discussed in detail and first order reaction model were used to determine the kinetic parameters for the pyrolysis of coal and pretreated biomass blend.

Final remarks are concluded in chapter 5. Suggestions and recommendations for future research directions are also outlined in this chapter.

Chapter 2

Literature Review

2. Literature Review

(In this chapter, previous work relevant to this study is quoted. Brief description of basic methods, theories and experimental work is also included in this chapter.)

These days, the expanding petroleum derivative costs and the worry for ecological maintainability speak to a critical overall challenge. Consequently, the inquiry and utilization of elective sources for energy is important, so as to limit the use of petroleum derivative and related issues [9]. As indicated by an evaluation of World Bank, the number of inhabitants in world has expanded by over 1.5 billion over the most recent 20 years [10]. In addition, the amount of the high position coal is constrained and the stores have been decreasing bit by bit, it is important to utilize low coal of low rank with enhanced technology [11].

Biomass has turned out to be a successful vitality bearer equipped for satisfying the developing interest of perfect and everlasting vitality hotspot for the feasible improvement of society [12]. Biomass is one of the promising types of perfect and green fuel that can meet everyday vitality necessities. Its use decrease the utilization of non-renewable energy sources, for example, coal, oil and petroleum gas [13].

Coal and biomass mix remove a portion of un-sustainable power sources and may prove as a best alternative to fulfill the earth demand for energy. Fuel creation from coal and biomass could be an option, economical and practical approach to utilize coal and biomass more productively [5]. Endeavors to create high-grade fuel from biomass and low position coal are vital from the perspective of sustainable power source and the usage of unused assets [8]. On the off chance that biomass is utilized with coal to generates energy, the ecological effect of petroleum product used, could be decreased and the carbon impression diminished [5]. Moreover, it is normal that a fuel delivered by blending both biomass and low position coal could counterbalance regular varieties in biomass supply by directing the blending proportion [14]. Furthermore, The use of biomass for vitality creation can decrease reliance on non-renewable energy sources [15]. Biomass is viewed as progressively feasible fuel because of its extremely low carbon impression and bottomless

accessibility at less expensive costs [16]. Pakistan being a farming nation with substantial yearly generation of agrarian waste, which can be utilized, for vitality creation [17].

Notwithstanding the different favorable circumstances of bioenergy as a perfect vitality source, it isn't being used at business levels because of the presence of different difficulties related with the biomass utilization at high level [12].

In any case, pretreatment could similarly assume a good job in upgrading thermochemical change of biomass into powers and synthetic concoctions. In this manner, there is developing enthusiasm for pretreating biomass into a reasonable feedstock before pyrolysis and gasification with the goal to improve quality and conversion productivity of biomass [6]. Toward this objective, pretreatment could be utilized to some degree as an apparatus to alter the organization/structure of biomass, into an appropriate feedstock that outcomes in less arrangement of unfortunate segments in charge of the impeding properties of pyrolysis products [18]. Biomass demineralization has shown to be a compelling procedure for diminishing the fouling and slagging nature of it, by lessening antacid and soluble earth metal substance and by improving fuel properties for high temperature works [1].

The trouble in creating compelling pretreatment of biomass is because of the presence cross linkages among lignin and hemicellulose and the crystalline structure of the cellulose in the wall of plant cell. A few physical as well as chemical pretreatment techniques are right now utilized to conquer the hard-headedness of lignocellulose, increment enzymes productivity and enhance the productivity of cellulose [19]. These pretreatment techniques incorporate acids (dilute or concentrated), bases, ammonia salts, heated water, organic solvents etc. [20].

A perfect pretreatment technique ought to be economically possible as well as ready to fractionate and recoup the vast majority of the significant synthetic segments i.e., hemicellulose, cellulose and lignin [21].

Organosolv pretreatment, then again, has tended to heaps of consideration because of the effectiveness of fractionating the biomass segments and the capability of increase production in the economical bio-refinery procedures [22]. Solvents that have been considered incorporate methanol, acetone, ethanol, ethylene glycol and glycerol etc. [23].

9

With the present accentuation on sustainable power source assets, the supply of glycerol is expanding quickly and is relied upon to make a genuine overproduction soon as biodiesel generation extends [24]. Being a high boiling natural organic compound, glycerol got from the oleochemicals business as a side product, has turned out to be exceptionally appealing. As of late, the taking off oil cost has made the oleochemicals business, particularly for biodiesel creation, all the more prospering, which makes glycerol production very high [25].

Organosolv pretreatment, being a novel technique, improved the cellulosic content of lignocellulosic biomass by expelling the lignin content and adjusting the physical structure present in biomass [26]. Organic solvent blend with some water, together with some catalyst like hydrochloric acid or sulphuric acid (HCl or H_2SO_4), separates lignin and hemicellulose linkages [23] [27]. In this way, the utilization of glycerol in organosolv pretreatment, can be viewed as a good and manageable option for the immediate usage of this modern side product from biodiesel industries [28]. Process variables like temperature, time, concentration of glycerol-aqueous solution etc. could be studied for glycerol pretreatment technology [29].

The transformation of biomass materials using thermochemical methods and their co-use with coal in energy production plants could decrease the amount of wastes and other hazardous products, considering vitality recuperation and give specialized, financial and natural advantages [30]. Pyrolysis being a conversion procedure or process, which permits the change of biomass into solid, liquid and gaseous items. The thermal disintegration investigation of the warm of coal and biomass is basic for evaluating their pertinence and for streamlining the pyrolysis procedure with the end goal of scaling up [31] [32].

There are numerous variables imperative for pyrolysis procedure, for example, temperature, weight, pressure, climate, rate of heating, minerals present, etc. [33] [34].

For the utilization of low position coal on high scale, kinetic models and pyrolysis characteristics are important factor to design and improve pyrolysis reactor [35]. Investigation on agriculture waste material demonstrated that biomasses are different kind of fuel in comparison to coal as for kinetic and thermal conduct in inert conditions [36].

Iso-conversional strategies are utilized to assess kinetic parameters, dependent on trials did at different heating rates, giving various kinetic parameters [31].

Ozawa in their investigation additionally defended that Flynn Wall Ozawa (F–W–O) technique is a progressively precise strategy and referenced that the amounts used to assess the activation vitality are more straightforward in F–W–O strategy contrasted with others [37]. Kinetic parameters in case of coal are different for pyrolysis at low temperature with various heating rate. In addition, activation energy as well as pre-exponential factor also increased with increase in heating rate [33].

Chapter 3

Materials and

Methods

3. Materials and Methods

(Materials used for experimental techniques adopted in this study are described in this chapter. The materials include Coal, Rice husk and Glycerol. The experimental techniques and equipment used for pretreatment, ultimate analysis, calorific value and thermogravimetric analysis are elaborated here in detail.)

3.1 Materials

Materials that are used in this study are Coal, Rice husk and Glycerol. Major characteristics of these materials are described in next sections.

3.1.1 Coal

Coal is a hard sedimentary rock, which is used to get energy by burning it in presence of oxygen. It is for the most part carbon yet additionally contains hydrogen, sulphur, oxygen and nitrogen. Coal was formed from plants, buried inside earth thousands years ago by the pressure of rocks laid over the plants. Under suitable conditions inside the earth, these buried plants were converted into coal following step wise conversion as follow:

➢ Plants to peat which is mixture of partially decomposed vegetation material.

➢ Peat into lignite which is also called brown coal mainly consist of 50-60% carbon and other chemical compounds. Lignite is also used as fuel in some areas for power generation.

➢ Lignite was then converted into sub-bituminous coal, which is dark brown, dense rock. Sub-bituminous coal contains high content of aromatic hydrocarbons.

➢ Bituminous coal was then formed, which is a dark rock with high percentage of carbon. Bituminous coal is soft and can be easily burned. Bituminous coal is usually used in power stations for generating energy.

➢ Anthracite, which is hardest, shiny black coal. It contains highest percentage of carbon in it and is difficult to burn as compared to bituminous coal. It last longer while burning and is therefore used for heating space in residential as well as commercial places.

Figure 3-1: Piece of bituminous coal.
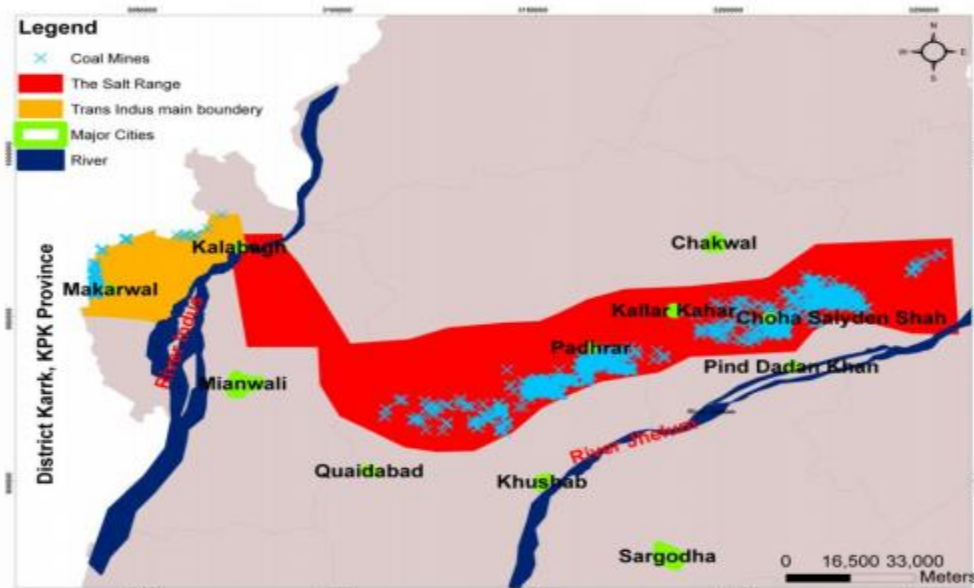
Figure 3-2: Coal mines in Surghar and Salt range in Punjab.

In Pakistan, huge resources of sub-bituminous and bituminous coal is present. Mines & Mineral Department, Government of the Punjab, conducted an estimation for local coal reserves of the Surghar and Salt Range (Trans-Indus) Range area on international JORC Standards with the help of Australian Consultant, Snowden (2010-2013). The report has

concluded that Surghar and Salt Range consist of almost 600 million tons of bituminous coal of Rank-D and approximately 800 small semi-operative coalmines are present there.

The Government of Punjab has been encouraging every such activity, which may prompt outside investment particularly in the space of foundation of nearby coal based power plants in these areas.

Coal used in this study is also from one of these areas, which is of Padhrar region, District Khushab, Province Punjab, Pakistan

3.1.2 Rice husk

The rice husk, additionally called rice body, is the covering on a seed or grain of rice. It is manufactured from hard materials, including silica, cellulose, hemicellulose and lignin, to secure the seed in the developing season. Every kilogram of processed white rice results in generally 0.28 kg of rice husk. When rice grain is separated from husk in rice processing mill, rice husk is obtained as a byproduct as shown in Figure 3-3. This obtained rice husk usually have no remarkable value and considered as waste.
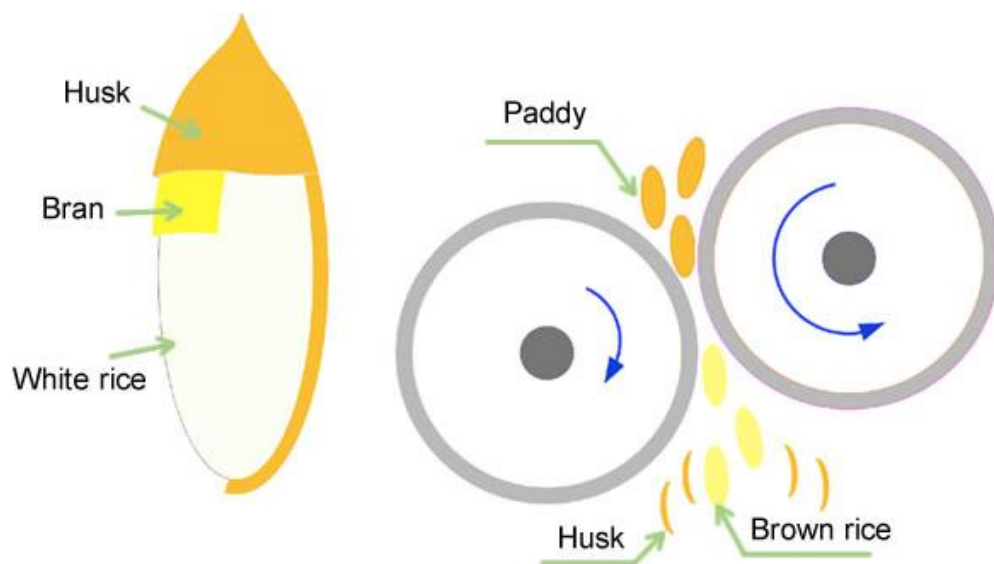
Figure 3-3: Paddy grain and its product after husking.

Pakistan being an agriculture country, produce major crops include wheat, rice, cotton, sugarcane, maize, etc. According to ministry of finance, rice production in 2014–2015 was 6900 thousand metric tons. Table 1 shows the amount of paddy and rice husk produced from year 2008-2015 in Pakistan. It can be seen that on average about 1828 thousand metric ton of rice husk is produced every year.

Table 1: Production of rice husk in Pakistan.

Year	Paddy production (1000 tons)	Rice husk (1000 tons)
2008	6952	1390.4
2009	6883	2064.9
2010	4823	1446.9
2011	6160	1848
2012	5536	1660.8
2013	6798	2039.4
2014	7005	2101.5
2015	6900	2070
Average	6382	1828

Rice husk used in this study is taken from a local industry located in Tehsil Wazirabad, District Gujranwala, Punjab, Pakistan.
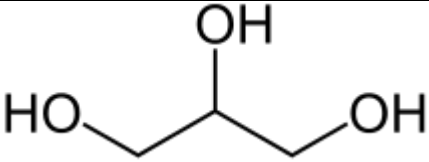
3.1.3 Glycerol

Glycerol also known as glycerin is a simple nontoxic organo-solvent compound having high boiling point (290°C) with no color, odor and sweet in taste. Glycerol is produced in a bulk quantity as a by-product from biodiesel industries. About 1.2 million ton of glycerol was produced in Europe in 2010 and its production goes on increasing with the rise in production of biofuels. Glycerol is not only available in bulk quantity but is also very cheap as compared to other organic solvent. Table 2 shows the physical and chemical properties of glycerol.

Figure 3-4: Sigma Aldrich Glycerol

Table 2: Physical and Chemical properties of glycerol.

Chemical name	1,2,3-Trihydroxypropane
Commercial name	Glycerol
Melting point	17.8˚C
Boiling point	290˚C
Molar mass	92 g/mol
Odor	Odorless
Chemical formula	$C_3H_8O_3$
Structural formula	
Density	1.261g/cm^3
Viscosity	1.412 Pa.s

Laboratory Glycerol from Sigma-Aldrich having percentage purity ≥99.5% is used for pretreatment purpose.

3.2 Methodology

The methodology followed to carry out this study is shown below in Figure 3-5 in the form of block diagram. The main steps include in the methodology are briefly described here. It starts with the grounding, screening and drying of raw coal and industrial lignocellulosic rice husk. Then pretreatment of industrial lignocellulosic rice husk with different proportion of glycerol G for a constant temperature and time (80˚C & 3 hours) in a water bath. Then pretreated industrial lignocellulosic rice husk is washed with water and dried. Then dried industrial lignocellulosic rice husk is mixed with coal and then prepared samples are subjected to different characterizations like proximate and ultimate analysis, Fourier transform infrared spectroscopy and thermogravimetric analysis. At the end, Flynn Wall Ozawa method is used to estimate activation energy for different c0al-biomass samples.

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┌─────────────────────┐
│   Grounding of raw  │
│   material (Coal &   │
│       biomass)      │
└─────────────────────┘
          ⇩
┌─────────────────────┐
│   Screening of raw  │
│       material      │
└─────────────────────┘
          ⇩
┌─────────────────────┐
│                     │
│       Drying        │
│                     │
└─────────────────────┘
          ⇩
┌─────────────────────┐
│   Pretreatment of   │
│       biomass       │
└─────────────────────┘
          ⇩
┌─────────────────────┐
│ Washing of pretreated│
│    lignocellulosic  │
│       biomass       │
└─────────────────────┘
          ⇩
┌─────────────────────┐
│                     │
│       Drying        │
│                     │
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          ⇩
┌─────────────────────┐
│   Mixing of biomass │
│      with coal      │
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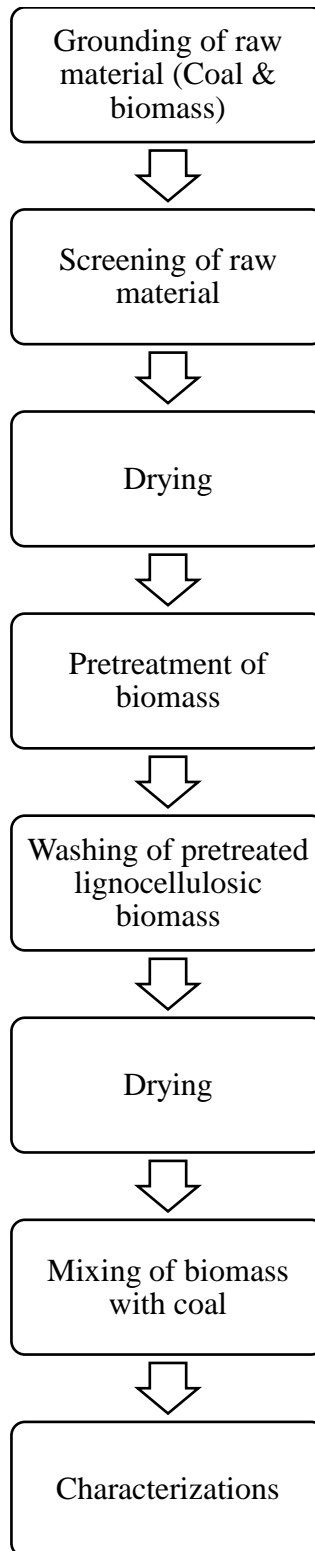
Figure 3-5: Block diagram of the methodology followed for this study.

3.2.1 Grounding of raw material (Coal & biomass)

Coal was taken form Padhrar coal reserves located in province Punjab of Pakistan. Rice husk was collected from the local rice industries. Coal was firstly ground in a ball mill and then in pebble mill to fine powder placed in Particle technology lab, UET Lahore, KSK campus. Rice husk was grinded in a ultrafine grinder placed in Chemical Process lab, UET Lahore, KSK campus.

3.2.2 Screening of raw material (Coal & biomass)

Coal and rice husk were screened using a CISA cedaceria BA200N sieve shaker to a particle size <500µm using sieve having mesh size of 35.

3.2.3 Drying

After screening, both coal and rice husk were kept in LabTech electric oven at 45˚C for a fortnight in order to remove any free moisture present.

3.2.4 Pretreatment of biomass (Rice husk)

Biomass (rice husk) was pre-treated with Laboratory Glycerol G from Sigma-Aldrich having percentage purity ≥99.5%. Four solutions having concentration 100% G, 75% G, 50%G and 25% G were made. Rice husk was mixed with these solutions in a ratio of 1:10 w/v rice husk to glycerol in 500ml beaker. After, these four samples were kept in a Memert orbital and reciprocating water bath WNB14 for three hours at 85˚C with a stroke rate of 160/min.

3.2.5 Washing of pretreated biomass (Rice husk)

After pretreatment, biomass was wash with distilled water in order to remove all glycerol from biomass particles.

3.2.6 Drying of pretreated biomass

After washing, treated biomass was kept in sunlight for 3-4 hours and then in oven at 45˚C for one night.

3.2.7 Mixing of biomass with coal

Treated biomass after drying was mixed with coal in a ratio of 1:1 w/w in order to make coal-biomass blends.

Sample of coal-biomass blend having untreated biomass was termed as RC, Sample of coal-biomass blend having treated biomass with 100% G solution was termed as RC1, Sample of coal-biomass blend having treated biomass with 75% G solution was termed as RC2, Sample of coal-biomass blend having treated biomass with 50% G solution was termed as RC3 and sample of coal-biomass blend having treated biomass with 25% G solution was termed as RC4.

3.3 Characterizations

Proximate and Ultimate analysis, GCV analysis, Chemical analysis, Fourier transform inferred spectroscopy and Thermogravimetric analysis are the characterization techniques that are used in this study. The important equipment specifications and the technical details of equipment are described in the next sections

3.3.1 Proximate analysis, Ultimate analysis & Gross Calorific Value GCV

Proximate analysis is used to determine the amount of volatile matter, moisture content and ash percentages, fixed carbon content etc. while ultimate analysis determines all coal component elements (carbon, hydrogen, nitrogen, sulphur and oxygen).

Proximate analysis was done at Chemical Process Industries lab, Department of Chemical, Polymer and Composite material Engineering UET KSK campus.

For determination of moisture content, samples are weighed and are kept in uncovered crucible in oven at 110˚C. Then the sample is cooled to room temperature and weighed again. The loss in weight represents moisture content.

For measurement of Volatile Matter, fresh sample of coal-biomass blend is weighed and placed in a covered crucible, and heated in a furnace at 900˚C. Loss of weight represents moisture and volatile matter. The remainder is coke (fixed carbon and ash).

For ash content, the cover from the crucible used in the last test is removed and the crucible is heated at 600˚C until all the carbon is burned. The residue is weighed, which is the incombustible ash. The difference in weight from the previous weighing is the fixed carbon. In actual practice Fixed Carbon or FC derived by subtracting from 100 the value of moisture, volatile matter and ash.

Ultimate analysis and Gross calorific value GCV determination was done at Center of Energy, Research and Development (CERAD) lab, Department of Chemical, Polymer and Composite material Engineering UET KSK campus. The equipment used for this purpose was LECO CHNS analyzer 628 and LECO Bomb Calorimeter AC500.

3.3.2 Fourier Transform Infrared Raidation Spectroscopy

FTIR spectroscopy analysis was done at research lab of Basic Science Department UET KSK Campus by using equipment "PerkinElmer UTAR Two". To check the functionality of equipment Polystyrene was used as reference material. The sensor was washed with methanol to remove the dust and impurities to have good results. Coal-biomass blend with untreated biomass was placed on the sensor and analysis was performed. Same process was repeated with other coal-biomass blends with treated samples and peaks were identified to evaluate the changes in all samples. Later comparison was done between coal-biomass blends having untreated and treated biomass content. The equipment is shown in Figure 3-8.

Figure 3-6: LECO 628 CHNS analyzer.

Figure 3-7: LECO AC 500 Bomb Calorimeter.

Figure 3-8: PerkinElmer UTAR FTIR Instrument.

3.3.3 Thermogravimetric Analysis

SDT-Q600 Thermal Analyzer (TA, as shown in Figure 3-9) is used to determine the loss in mass of sample with respect to time and temperature. It can analyze samples up to temperature 1500°C. This thermal analyzer is combination of Differential scanning calorimetry (DSC) and Thermogravimetric analyzer (TGA). The tests were performed under N_2 atmosphere with heating rate of 10, 30 and 40°C/min up to the temperature of 900°C.

Thermogravimetric analyzer measures mass with increase in temperature of sample continuously with time, these three (mass, temperature and time) measurements are considered as base measurements and other additional calculations may be deduced from these. It is used for characterization of different materials especially coal and biomass through investigation of characteristic decomposition patterns.

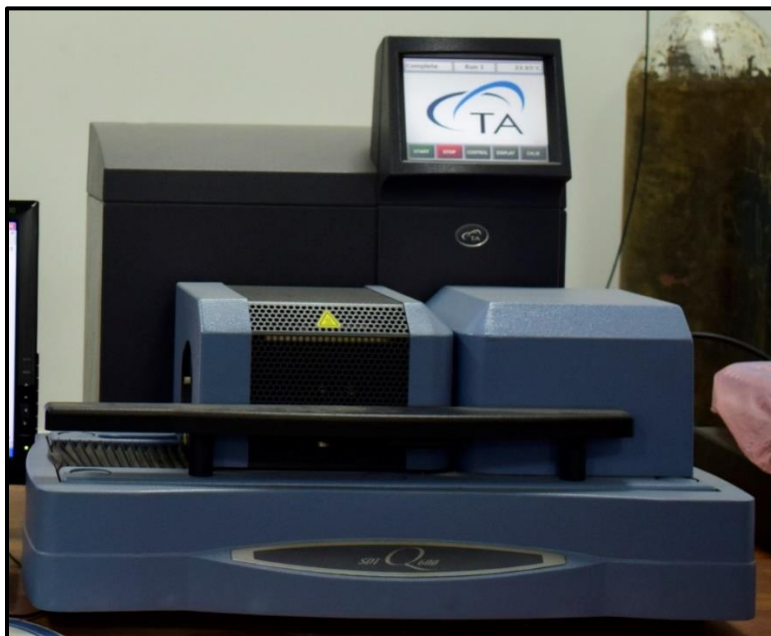Figure 3-9: SDT Q600 Thermogravimetric Analyzer.

This analyzer contains a precision balance with an aluminum pan for sample loading, placed inside of a furnace with temperature controller (programmable control temperature). The precision balance works on the mechanism of dual balance with the sensitivity of 0.1µg. Platinum type thermocouple is placed in furnace with ceramic beam that can record

temperature readings up to 1500°C. Sample capacity is 350mg that can be loaded in the aluminum pan and about 10mg sample is used for analysis. Gas purge system has a role in control of mass flowrate and ensure no back diffusion and efficient removal of decomposed products from sample. The constant rate of temperature increase is kept to incur the thermal reaction that can occur under ambient air and inert atmospheres.

3.3.4 Chemical Analysis

Chemical analysis was done in order to determine percentage of cellulose, hemicellulose and lignin present in the raw and pretreated rice husk.

Cellulose percentage of crude and pretreated rice husk material was resolved utilizing cellulose seclusion technique. An acidic-nitric corrosive reagent, which comprises of acetic and nitric acid in a proportion of 10:1 (v/v) and percentage purity of 80% was prepared. Test tubes was washed and dried completely. 0.1 gram of rice husk (untreated & treated samples) was taken into dried test tubes. Then, 3 ml of acidic/nitric reagent was included into each test tube and was blended vivaciously. After, test tubes were covered and placed in boiling water for about 30 minutes. When finished, the test tubes were taken out and allowed to be cool down by adding 10 ml of deionized water in the each test tube. The reaction with acidic-nitric reagent effectively expelled lignin and hemicellulose present in the RH samples, deserting cellulose in the blend which was collected by separating the solution utilizing vacuum filtration arrangement.

The hemicellulose content percentage present in the rice husk RH samples was acquired by the distinction between the holocellulose and cellulose substance. Thusly, holocellulose, which is the entirety of cellulose and hemicellulose in the biomass, was first obtained by the sodium chlorite strategy. 0.5 g of the RH sample was treated with 30 ml of deionized water, which contains a minute quantity of acetic acid (0.04 ml) and 0.4 g of sodium chlorite ($NaClO_2$) at 75°C for 1 hour. Also, 0.2 g of sodium chlorite and 0.04 ml of acid were added to the blend each 1 hour for 3 hours. When finished, the buildup was separated, washed with distilled water, and after that dried consistent weight for one night. The solid material or deposit acquired after the response of RH with sodium chlorite in acetic acid derivation medium contains holocellulose content in it and hemicellulose percentage

content was measured by getting difference in values among holocellulose percentage content and cellulose percentage content.

The lignin percentage content present in the raw and pretreated rice husk RH was dictated by utilizing two step, advance corrosive hydrolysis with acitd. Right off the bat, 1.5 ml of sulphuric acid (72% w/w) was added to 0.10 g of RH sample in a 50 ml cone shaped flask. Hydrolysis was completed in a water bath shaker for 2 hours at 30˚C and 150 rpm. When completed, deionized water (56ml) was added to weaken the acid solution to a last 4% concentration (w/w). After this, second step hydrolysis was done via autoclaving the response blend at 120˚C and 2 atm pressure in an autoclave for 1 hour. The strong buildup residues staying after the two-advance hydrolysis was obtained by vacuum filtration and was dried for one night in an electric oven to consistent weight.

3.3.5 Kinetic study and activation energy

Thermogravimetric investigations have been utilized for studying the thermal degradation of the coal-biomass blends. In previous decade, an expanding number of kinetics investigations have been conducted utilizing TGA data for deciding activation energy, rate constants, order of reaction and Arrhenius exponential constants.

Basic rate equation is given by:

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

Where,

dα/dt is the conversion rate at a fixed temperature, k is the rate constant, f(α) is the reaction model and α is rate of conversion which is given by:

$$\alpha = \frac{Wo-Wt}{Wo-Wf} \tag{2}$$

Where, W_t, W_o and W_f are the time t, initial and final weights of the sample.

For the study of coal-biomass degradation, it can be assumed that conversion rate is proportional to reacting material concentration, which gives,

$$f(\alpha) = (1 - \alpha)^n \tag{3}$$

25

Where, n is order of reaction. Heating rate in TGA is also used for kinetic study.

$$\beta = \frac{dT}{dt} \tag{4}$$

Where, β represents the heating rate and dT/dt represents change in temperature with respect to time.

From Arrhenius equation, rate constant k is given by:

$$k = A.\exp(\frac{-E_a}{RT}) \tag{5}$$

Where, E_a is activation energy, A is exponential factor, T is temperature and R is gas constant. Combining equation 1 to 5 we'll get,

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} . \exp\left(\frac{-E_a}{RT}\right) . dT \tag{6}$$

Equation (6) represents the most basic equation, which was used for kinetic parameter studying utilizing TGA data. Activation energy E_a can be evaluated from different models which are describe in Table 3.

Table 3: Different methods utilized for evaluating kinetic parameters.

Method	Expressions	Plots
Kissinger	$\ln\left\{\frac{\beta}{T_p^2}\right\} = \ln\left\{\frac{AR}{E_a}\right\} + \left\{\frac{1}{T_p}\right\}\left\{\frac{-E_a}{R}\right\}$	$\ln\left\{\frac{\beta}{T_p^2}\right\}$ against $\frac{1}{T_p}$
Fried man	$\ln\frac{d\alpha}{dt} = \ln[Af(\alpha) - \frac{E_a}{RT}$	$\ln\frac{d\alpha}{dt}$ against 1/T
Flynn and Wall	$\frac{-dlog\beta}{d(\frac{1}{T})} = 0.457\frac{E_a}{R}$	$-dlog\beta$ against 1/T
Flynn-Wall-Ozawa	$logF(\alpha) = log\left\{\frac{AEa}{R}\right\} - log\beta - 2.315$ $- 0.4567\frac{Ea}{RT}$	Log β against 1/T for a fixed degree of conversion

Chapter 4

Results and

Discussion

4. Results and Discussion

(In this chapter, the effect of glycerol pre-treatment on biomass present in coal-biomass blends was examined by using activation energy approach determine by Flynn Wall Ozawa method, which tells about the thermal stability and efficiency of fuel. The effect of glycerol pre-treatment on percentage content of cellulose, hemicellulose and lignin was also determined here. Gross calorific value and percentage of Carbon, hydrogen, nitrogen, sulphur and oxygen is also determined using ultimate analysis.)

4.1 Proximate and Ultimate analysis

Table 4 shows the result for proximate and ultimate analysis of pure coal, rice husk and coal-biomass blends with untreated and treated biomass. In the case of moisture content, it can be seen that pure rice husk has the highest percentage of moisture content while pure coal has the least amount. For V.M the trend is opposite as for M.C. Here, pure coal has the highest value. It can be seen that percentage of V.M is slightly higher in coal-biomass blend with treated biomass as compared to the blend with untreated biomass. Also, ash content of blends with treated biomass is lower as compared to the untreated one. Fixed carbon percentage is highest in the blend having biomass treated with 75% glycerol solution. Percentage of elemental carbon C and hydrogen H is highest in blend which have treated biomass with 100% glycerol G, while percentage of nitrogen N and sulphur S is lowest in this blend. Gross calorific value GCV is highest in the blend having biomass treated with 75% glycerol solution.

4.2 Chemical Analysis

Table 5 demonstrates the percentage content of cellulose, hemicellulose and Lignin+ash present in untreated and treated rice husk RH.

From table, it can be seen that cellulose percentage is least in untreated rice husk RH while percentage of lignin and hemicellulose is highest in it. However, in case of treated rice husk, percentage of cellulose is increased to a sufficient extent and percentage of lignin and hemicellulose is decreased. Cellulose content is maximum for the rice husk treated with 100% glycerol G.

Table 4: Proximate and Ultimate analysis.

	Coal	Rice Husk	RC	RC1	RC2	RC3	RC4
Moisture (%)	5.3	6.5	6.1	6.3	6.4	5.8	6.4
V.M (%)	36.6	14.0	21.7	22.5	20.7	22.8	22.9
Ash (%)	29.9	12.7	22.9	22.3	20.3	19.5	18.8
Fixed Carbon %	28.2	66.7	49.3	48.9	52.6	51.9	51.9
Carbon (%)	37.03	39.275	38.156	41.894	41.009	41.196	40.515
Hydogen (%)	4.1242	6.262	5.0729	5.3996	5.1473	5.1954	5.0877
Nitrogen (%)	7.6805	12.037	12.937	10.554	11.144	11.465	11.748
Sulphur (%)	6.351	0.2008	2.694	2.185	2.687	3.346	3.163
Oxygen (%)	44.814	42.225	41.140	39.967	40.012	38.797	39.486
Gross calorific value GCV (cal/g)	4335.35	3801.05	4012.13	4052.28	4072.1	4063.63	4044.5

Table 5: Percentage of Cellulose, Hemicellulose & Lignin+ash in untreated and treated rice husk.

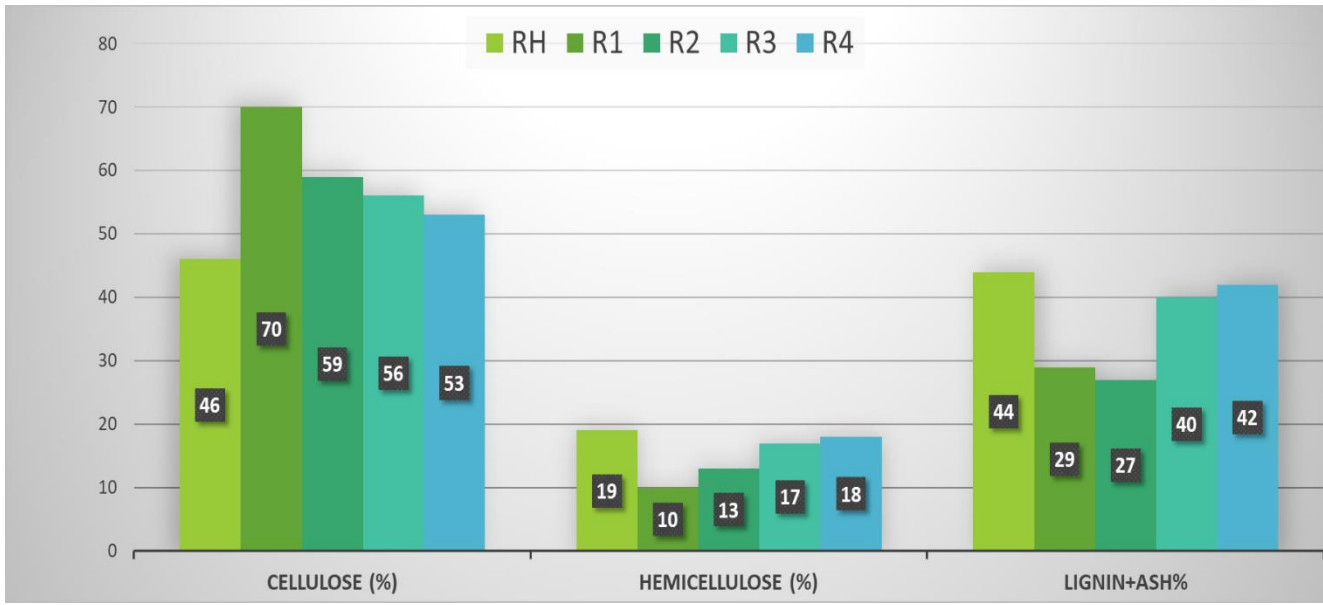|	RH	R1	R2	R3	R4
Cellulose (%)	46	70	59	56	53
Hemicellulose (%)	19	10	13	17	18
Lignin+Ash%	44	29	27	40	42

Figure 4-1: Percentage of Cellulose, Hemicellulose & Lignin+ash in untreated and treated rice husk.

4.3 Fourier Transform Infrared Radiation Spectroscopy

Figure 4.1 represents results for Fourier Transform Infrared Radiation Spectroscopy FTIR on coal-biomass blend with untreated and treated biomass. FTIR helps in understanding the chemical changes brought about by the chemical treatment of industrial lignocellulosic waste biomass. In figure 4.1, the peaks at 1760 cm-1 and 1680 cm-1 represents to –C=O vibrations of carbonyl group present in hemicellulose and –C=C– stretching present in
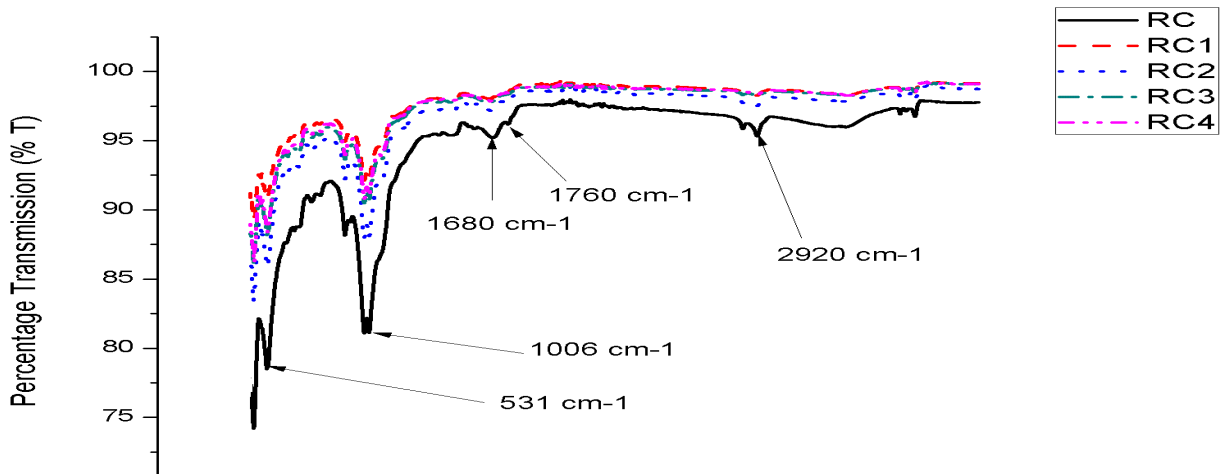

Figure 4-2: FTIR spectrum of coal-biomass blend with untreated and treated biomass.

lignin content respectively. The hemicelluloses content is partially removed from the biomass after its treatment, as apparent of diminished in carbonyl peak at 1760 cm-1. In addition, there is a decrease in peak at 1680 cm-1 in pretreated biomass samples, which shows the removal of lignin content.

4.4 Thermogravimetric analysis

Figure 4-3, 4-4 & 4-5 shows the thermogravimetric curves (temperature vs weight %) and DTG curves (temperature vs derivative weight) of coal-biomass blends with untreated and treated biomass at a heating rate of 10, 30 and 40˚C/min. TG curves can be divided into three regions. In first region, from 30-120˚C moisture present in the coal-biomass is evaporated. In second region, which is from 200-400˚C decomposition of cellulose and hemicellulose is happened. Rate of weight loss is maximum in the second region, which shows the increase in pyrolysis rate. Third region, which is from 400-600˚C for case of heating rate 10˚C/min and 400-700˚C for case of heating rate 30 and 40˚C/min represent the degradation of coal and lignin present in biomass. Coal at low temperature shows low degradation because of covalent bond between carbon atoms. On the other hand, lignocellulosic biomasses mainly consist of cellulose, hemicellulose and lignin, therefore, there de-volatilization temperate is between 150-350˚C for hemicellulose and 250-400˚C for cellulose. It can also be seen from the figure that thermal degradation of coal-biomass blend with treated biomass is improved and blend with treated biomass are more thermally stable as compared to the untreated one. It is because of increase in cellulose content present in biomass after treatment with glycerol. Also, some alkali and alkaline earth metals which catalysis the decomposition process is removed in case of treatment with glycerol water solution. It can also be observed that DTG curves of coal-blends with treated biomass is slightly shifted to right which indicated the increase in maximum temperature T_{max} as shown in Table 6. Also, amount of residue at 550˚C is increased for coal-biomass blend having treated biomass, which indicates improvement in thermal stability of blends with treated biomass.
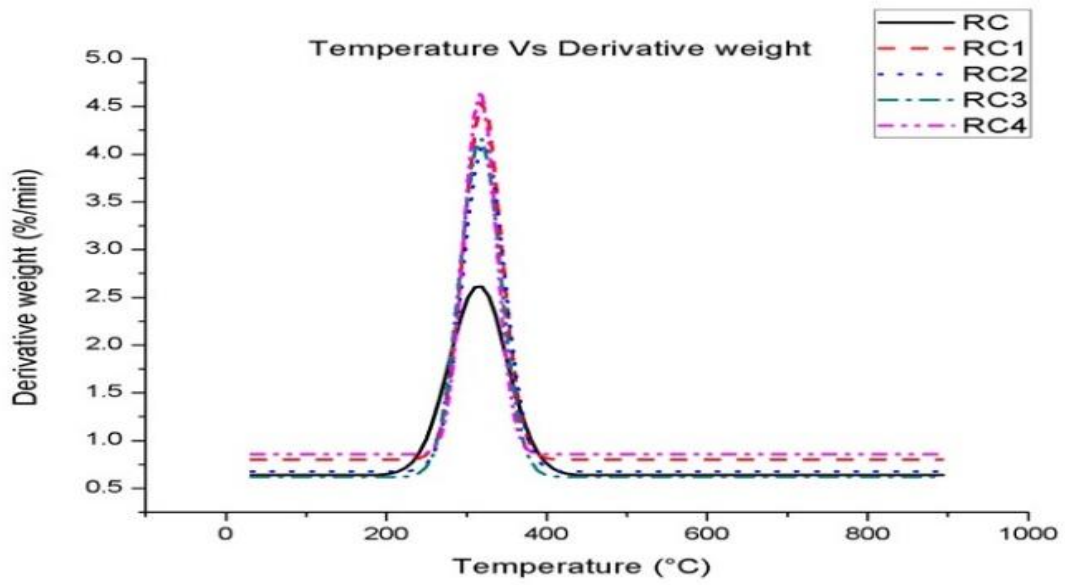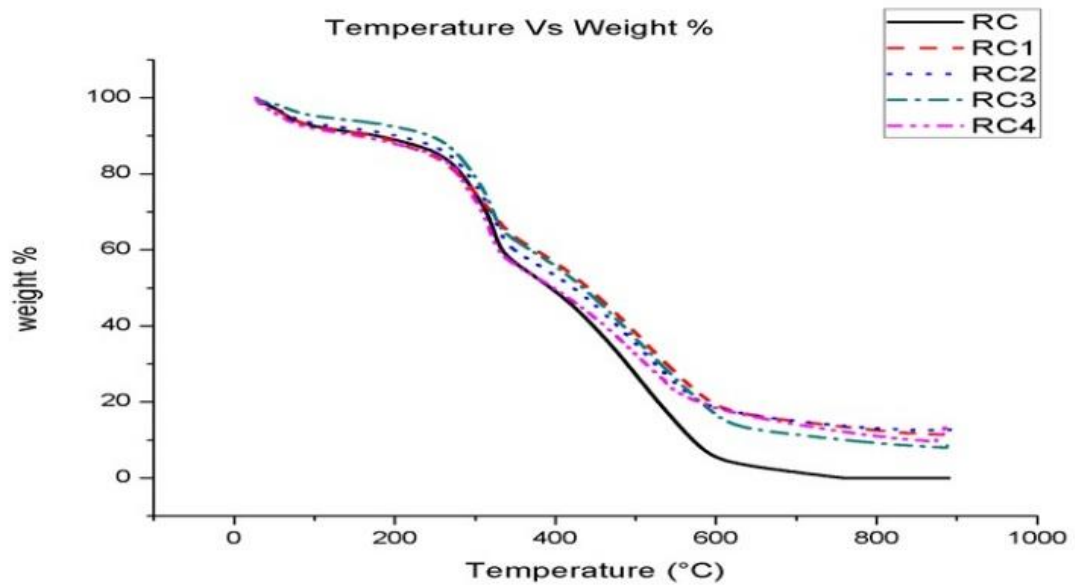
Figure 4-3: TGA & DTG curves for coal-biomass blends with treated and untreated RH at 10°C/min.
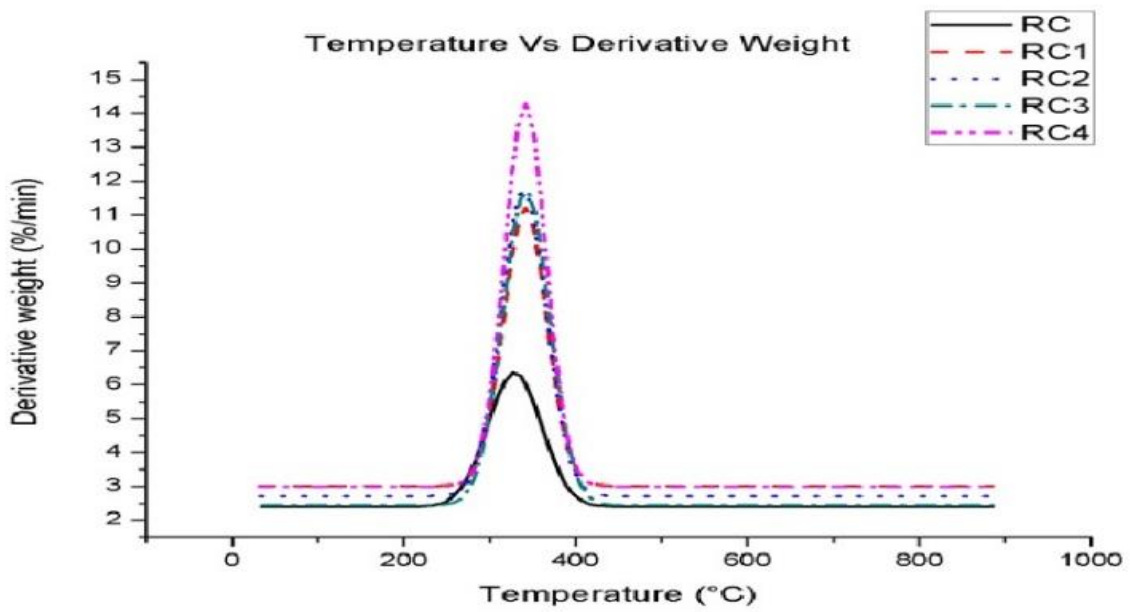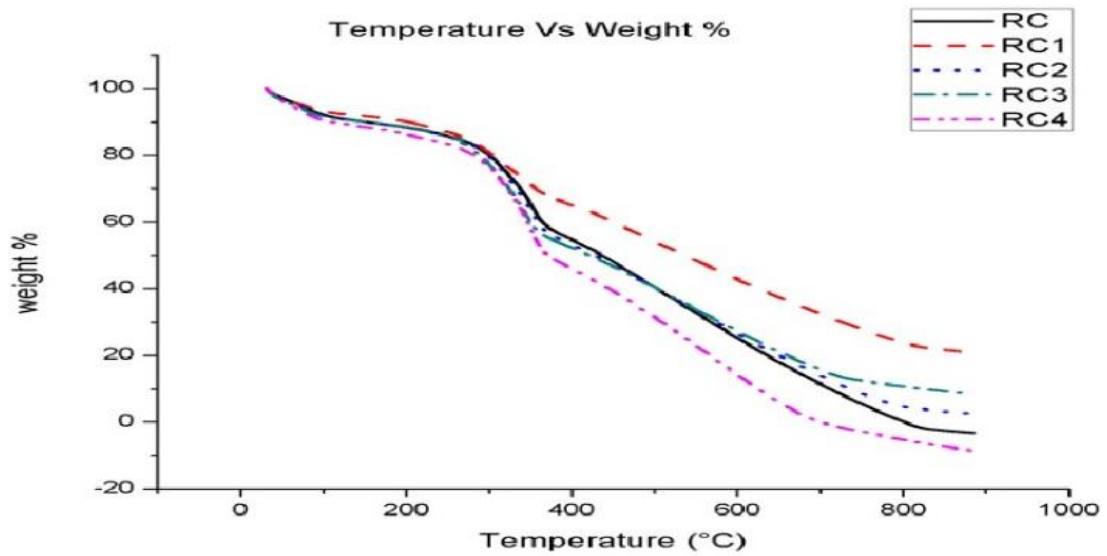
Figure 4-4: TGA & DTG curves for coal-biomass blends with treated and untreated RH at 30˚C/min.
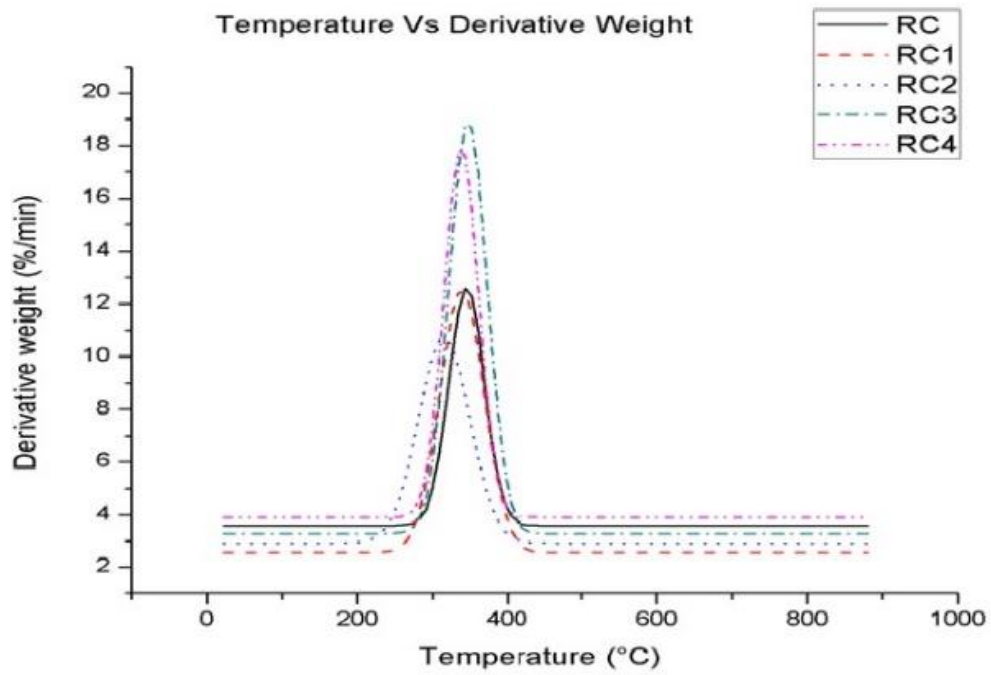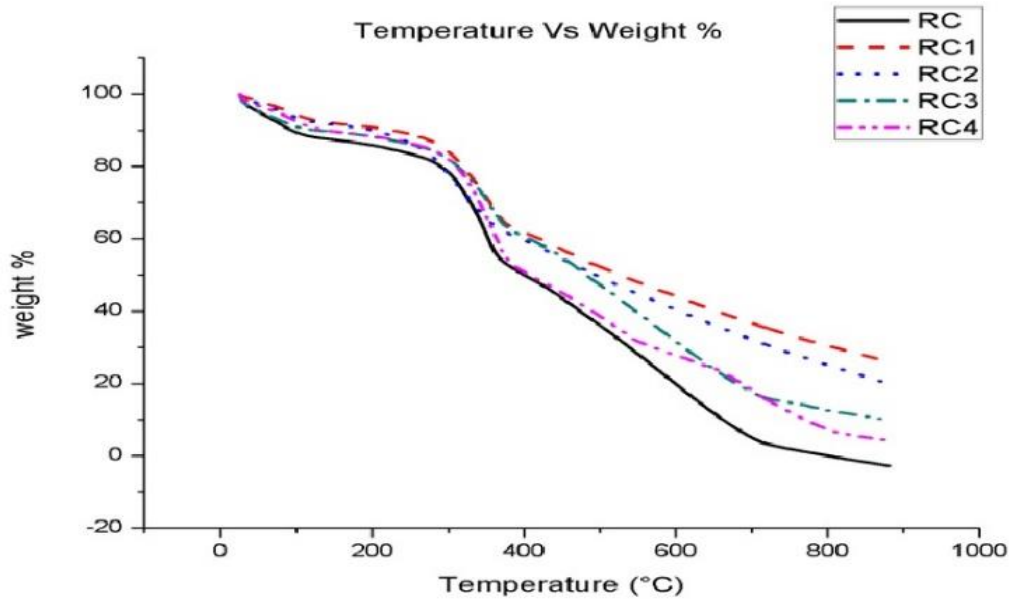
Figure 4-5: TGA & DTG curves for coal-biomass blends with treated and untreated RH at 40˚C/min.

Table 6: Thermal properties if coal-biomass blends with untreated and treated biomass.

Sample name	10˚C/min			30˚C/min			40˚C/min		
	T10 (˚C)	Residue at 550˚C (Weight %)	Tmax (˚C)	T10 (˚C)	Residue at 550˚C (Weight %)	Tmax (˚C)	T10 (˚C)	Residue at 550˚C (Weight %)	Tmax (˚C)
RC	173.46	14.74	322.513	152.76	32.66	340.671	106.2	28.12	350.7709
RC1	178.26	28.67	326.3262	207.11	48.73	353.2992	228.58	48.24	357.5007
RC2	205.24	27.72	328.9634	160.21	33.61	353.4326	210.48	45.6	355.556
RC3	244.17	27.64	326.5798	158.87	35.44	352.8466	170.7	38.98	353.394
RC4	154.04	24.77	326.2044	138.01	23.27	350.4804	131.28	23.22	352.1805

4.5 Kinetic study and Activation energy of thermal degradation:

In this study, average activation energy of thermal degradation was calculated from the conversion range of 0.1–0.7 through iso-conversional Flynn-Wall-Ozawa F–W–O method for both untreated and treated samples of coal and biomass blends at different heating rates of 10, 30 and 40˚C/min. Flynn–Wall–Ozawa is an integral method, which gives -E_a/R from the slope of the line obtained by plotting logβ against 1/T at any conversion rate.

Flynn-Wall-Ozawa eq. is given by:

$$logF(\alpha) = \log\left\{\frac{AEa}{R}\right\} - log\beta - 2.315 - 0.4567\frac{Ea}{RT}$$

Figure 4-6, 4-7, 4-8, 4-9 & 4-10 are the plots between logβ against 1/T for the conversion rate of 10-70% of coal blends with untreated and treated biomass. Activation energy was obtained by the slope of line plots between logβ and 1/T for various conversion percentage. Table 7 shows the activation energy of coal blends with untreated and treated biomass.

Coal and biomass being a solid fuel consist of many organic and inorganic compounds present in form of blends in it. Different chemical reactions occurs at a same time in order to decompose these compounds mixture present in coal and biomass. Due to complex structure of biomass, more unpredictably is added in case of coal and biomass decomposition. Therefore, activation energy varies with α during decomposition of coal-biomass blends.

In this study, coal-biomass blend with treated biomass show high activation energy as compared to the blend with untreated biomass due to increase in FC and cellulose content. Among blends with treated biomass, RC2 shows the highest activation energy. Kinetic study determined using Flynn Wall Ozawa method shows that average activation energy of blends with treated biomass is increased from 169.13 KJ/mol to 198.51 KJ/mol which shows that amount of energy required to break different bond present in blend with treated biomass is higher as compared to the blend with untreated biomass resulting in enhancement of thermal stability of coal biomass blend with treated biomass.

Figure 4-6: Plot of log β Vs 1/T for coal-biomass blends with untreated biomass.

Figure 4-7: Plot of log β Vs 1/T for coal-biomass blends with 100% glycerol treated biomass.

Figure 4-8: Plot of log β Vs 1/T for coal-biomass blends with 75% glycerol treated biomass.

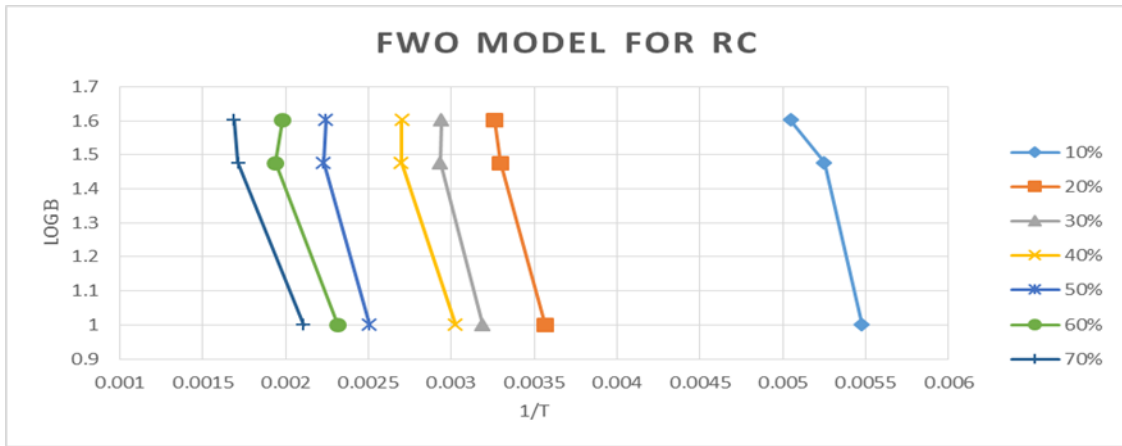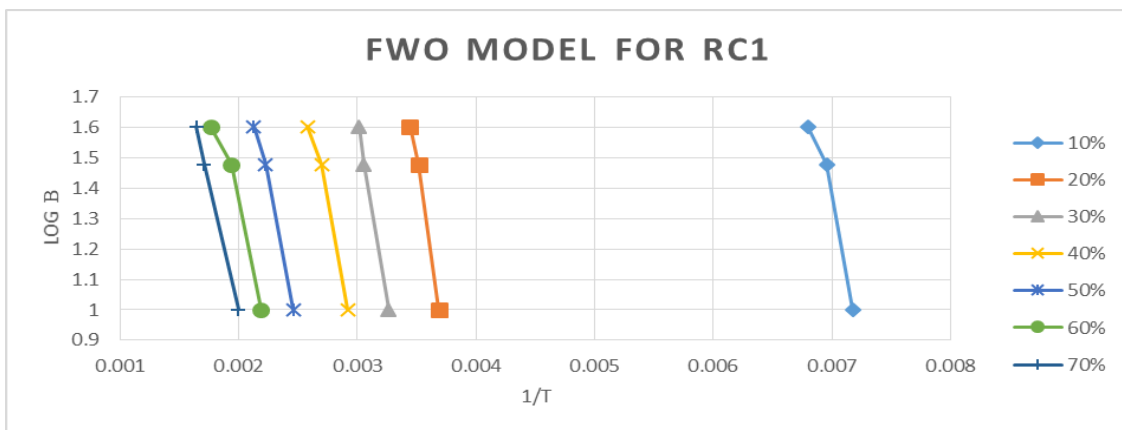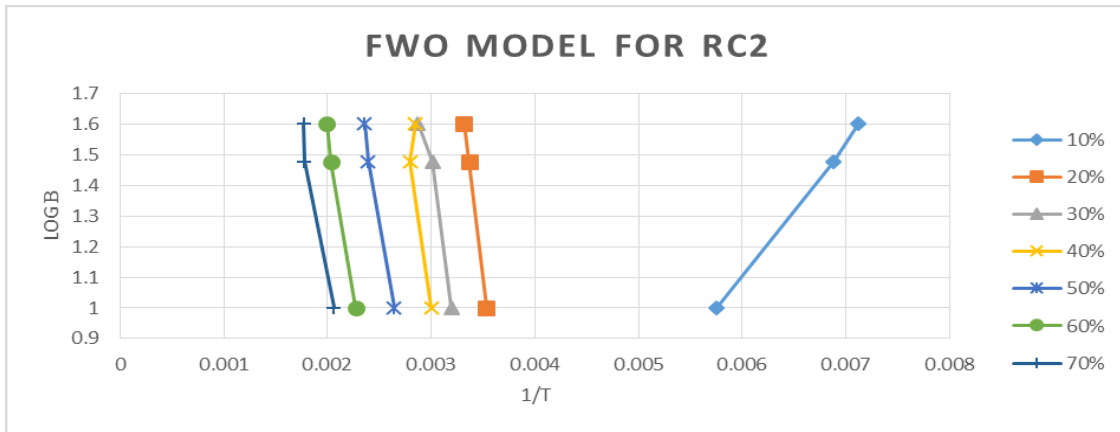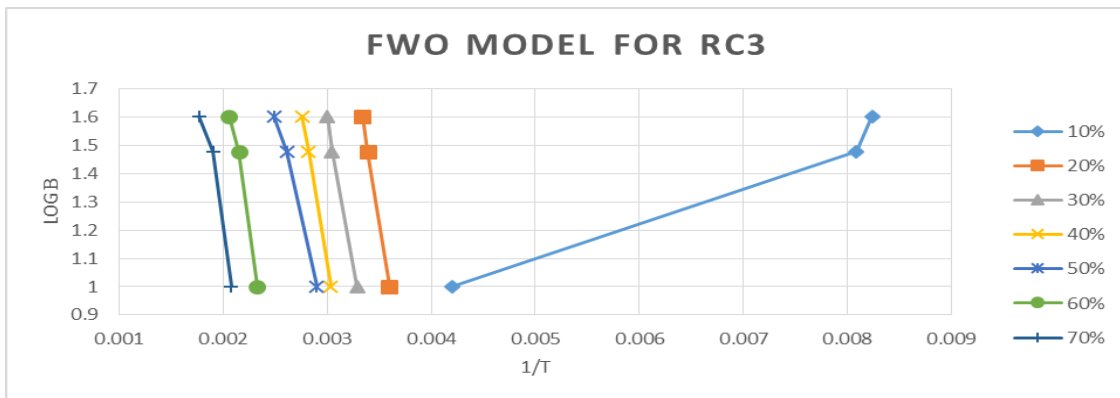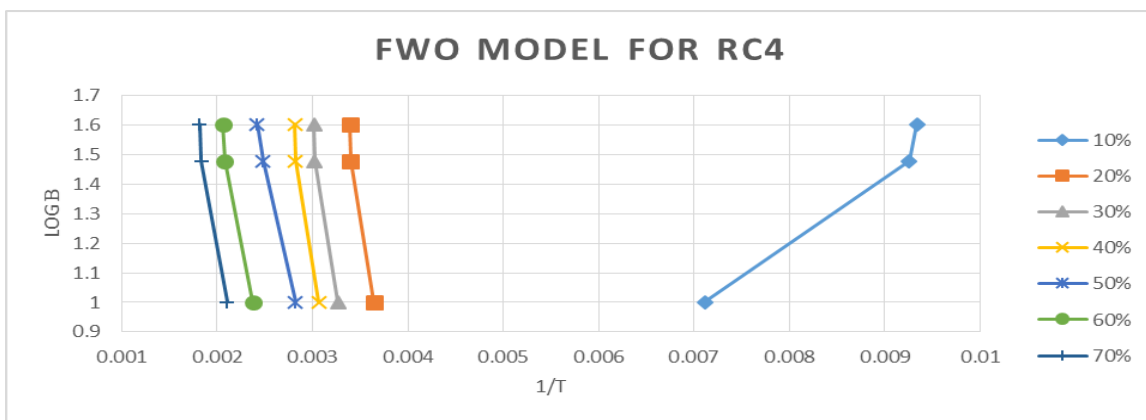Figure 4-9: Plot of log β Vs 1/T for coal-biomass blends with 50% glycerol treated biomass.

Figure 4-10: Plot of log β Vs 1/T for coal-biomass blends with 25% glycerol treated biomass.

Table 7: Activation energy and R^2 value for coal-biomass blends with untreated and treated biomass.

| Conversion rate %	RC		RC1		RC2		RC3		RC4	
	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2
10	141.46	0.916	162.98	0.948	43.49	0.998	13.71	0.973	24.84	0.973
20	188.32	0.991	250.37	0.9384	286.15	0.999	231.8	0.99	216.82	0.962
30	210.4	0.952	240.48	0.9981	188.3	0.938	207.19	0.997	218.36	0.9692
40	165.58	0.957	183.95	0.9731	269.2	0.8193	219.7	0.998	220.2	0.9743
50	198.1	0.943	186.92	0.99	205.04	0.992	148.58	0.988	148.24	0.997
60	147.0	0.91	145.69	0.951	208.13	0.994	230.6	0.9755	179.48	0.9803
70	133.03	0.979	167.72	0.99	189.23	0.9653	198.31	0.935	191.43	0.9788
Average Activation Energy (kJ/mol)	169.13		191.16		198.51		178.56		171.33	
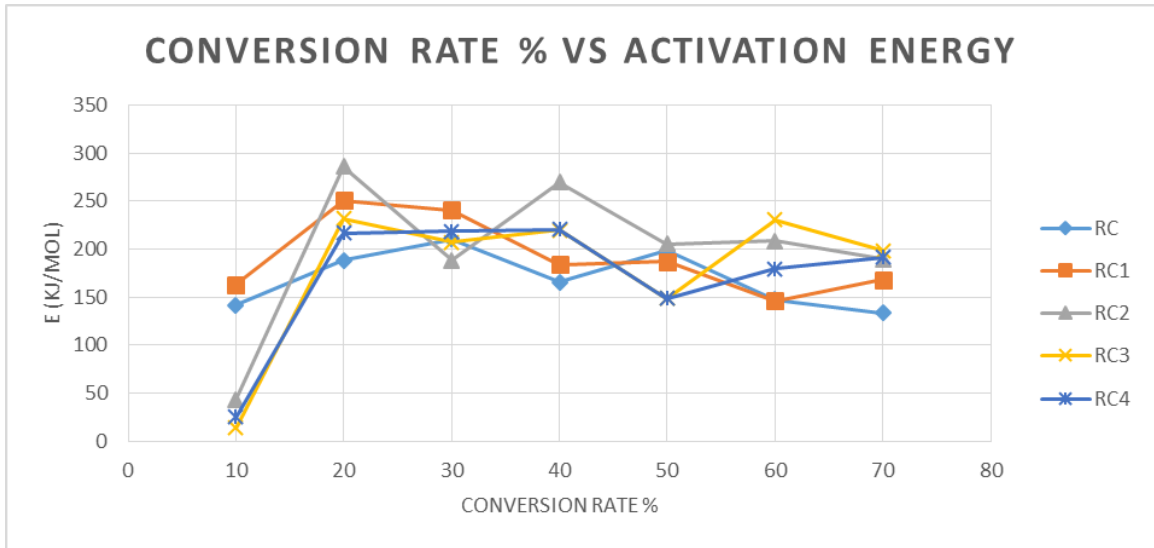
Figure 4-11: Variation of activation energy with fractional conversion α for coal-biomass blends with untreated and treated biomass.
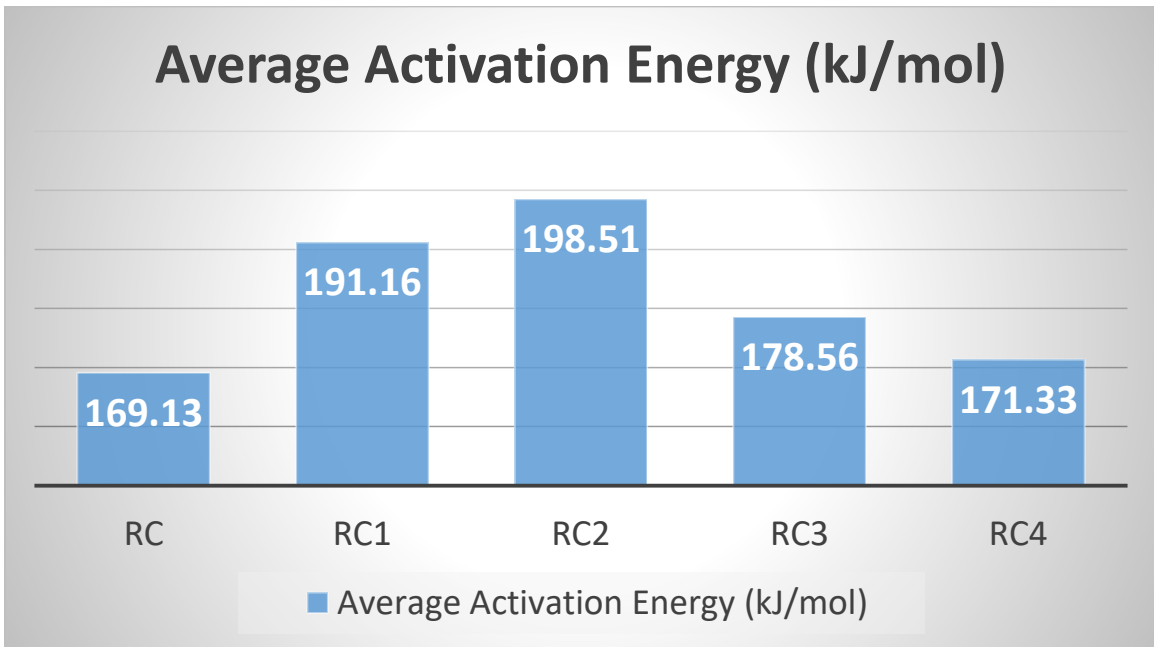

Figure 4-12: Average value of activation energy E for coal-biomass blends with untreated and treated biomass.

Chapter 5

Conclusions

5. Conclusion

(Herein, final deductions from this research work has been stated. It also includes some recommendations or future works that can be performed for additional studies.)

The main objective of this research was to study the effect of pretreatment of glycerol in different proportion on industrial lignocellulosic waste rice husk mixed with low quality coal available in Pakistan using approach of activation energy. From all the experimental work and results obtained from various characterization techniques, it can be concluded that percentage of volatile matter, carbon & hydrogen is increased in biomass-coal blends after pretreatment of biomass with glycerol while content of nitrogen, sulphur and ash is decreased obtained using Proximate and Ultimate analysis. Also, the value for GCV determined by using bomb calorimeter is increased after treatment. From chemical analysis, it's obvious that amount of cellulose present in rice-husk is increased after treatment with glycerol and lignin content is decreased. Lignocellulosic waste materials mainly composed of cellulose, hemicellulose and lignin with some other inorganic elements. The amount of cellulose is maximum in rice husk R2, which is treated with 75% glycerol and remaining water. In the case of coal-biomass blends with treated biomass, TGA analysis shows that there thermal stability is improved as compared to the blend which contains untreated biomass. And the blend of biomass which is treated with higher concertation of glycerol i.e. RC1 and RC2 shows maximum thermal stability as compared to the other samples. In addition, the T_{10}, T_{max} and residue at 550˚C for coal-biomass blends with treated biomass is also increased and this change is most prominent in case of RC2. Kinetic study determined using Flynn Wall Ozawa method shows that average activation energy of blends with treated biomass is increased from 169.13 KJ/mol to 198.51 KJ/mol which shows that amount of energy required to break different bond present in blend with treated biomass is higher as compared to the blend with untreated biomass resulting in enhancement of thermal stability of coal biomass blend with treated biomass. Therefore, activation energy obtained by using thermal degradation data could be a good technique in order to comprehend change in thermal stability & subsequent bond energy of coal-biomass blends with treated and untreated biomass. Glycerol being a cheap, thermally more

stable and readily available solvent is a good choice in order to pretreat lignocellulosic waste materials in order to enhance their properties.

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5.1 Future Work

This research has a wide scope and many other aspects can be further premeditated in future such as:

- Temperature of solvent (Glycerol) used for pretreatment of biomass could be vary and kinetic study parameters could be obtained.
- Some acid or base could be used as a catalyst during pretreatment of biomass.
- Same procedure could be apply on other biomasses like wheat straw, bagasse etc. and thermal stability could be obtained.
- Blends with different proportions of coal and pretreated biomass could be formed.
- Treatment time for biomass with glycerol solutions could be alter in order to study effect of time on thermo-chemical kinetics.

References:

[1]   Umair Aslam, Naveed Ramzan, Tanveer Iqbal, "Effect of demineralization on the physiochemical structure and thermal degradation of acid treated indigenous rice husk," P. Journal and C. Technology, pp. 1–6, 2016.

[2]   B. Neminda, S. Gan, C. Eastwick, and H. Kiat, "Biomass as an energy source in coal co- fi ring and its feasibility enhancement via pre-treatment techniques," *Fuel Process. Technol.*, vol. 159, pp. 287–305, 2017.

[3]   A. Kumar, P. Gupta, T. Goyal, and R. Kumar, "Modelling of pyrolysis of coal – biomass blends using thermogravimetric analysis," Bioresource Technology, vol. 99, pp. 8022–8026, 2008.

[4]   K. Lu, W. Lee, W. Chen, and T. Lin, "Thermogravimetric analysis and kinetics of co-pyrolysis of raw / torrefied wood and coal blends," *Appl. Energy*, vol. 105, pp. 57–65, 2013.

[5]   J. W. Qingzheng Cheng, Brian Via, "Primary Study of Woody Biomass and Coal for Energy Production Investigated by TGA-FTIR Analysis," 2015, 2014.

[6]   P. Harmsen, W. Huijgen, L. López, and R. Bakker, "Literature Review of Physical and Chemical Pretreatment Processes for Lignocellulosic Biomass," *Food Biobased Res.*, pp. 1–49, 2010.

[7]   V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, and D. B. Levin, "Biomass pretreatment : Fundamentals toward application," *Biotechnol. Adv.*, vol. 29, pp. 675–685, 2011.

[8]   M. Nonaka, T. Hirajima, and K. Sasaki, "Upgrading of low rank coal and woody biomass mixture by hydrothermal treatment," *Fuel*, vol. 90, pp. 2578–2584, 2011.

[9]   S. Abbas, A.; Ansumoli, "Global potential of rice husk as a renewable feedstock for ethanol biofuel production.," *Bioenergy Res.*, vol. 3, pp. 328−334, 2010.

[10]   Worldbank., "The Future of the World's Population in 4 Charts.," 2015.

[11]   H. Song, G. Liu, J. Zhang, and J. Wu, "Pyrolysis characteristics and kinetics of

low rank coals by TG-FTIR method," *Fuel Process. Technol.*, 2016.

[12] S. K. Sansaniwal, M. A. Rosen, and S. K. Tyagi, "Global challenges in the sustainable development of biomass gasi fi cation : An overview," *Renew. Sustain. Energy Rev.*, vol. 80, pp. 23–43, 2017.

[13] F. M. Pathak B, Chaudhari S, "Biomass–resource for sustainable development.," *Int J Adv Res Technol*, pp. 271–87, 2013.

[14] T. A. Lester E, Gong M, "Method for source apportionment in biomass/ coal blends using thermogravimetric analysis.," *J Anal Appl Pyrolysis*, pp. 111–117, 2007.

[15] A. A. Yorulmaz SY, "Investigation of combustion kinetics of treated and untreated waste wood samples with thermogravimetric analysis.," *Fuel Process Technol*, pp. 939–946, 2009.

[16] I. K. Idris SS, Rahman NA, "Combustion characteristics of Malaysian oil palm biomass, sub-bituminous coal and their respective blends via thermogravimetric analysis (TGA).," *Bioresour Technol*, pp. 581–591, 2012.

[17] M. T. Mirza UK, Ahmad N, "An overview of biomass energy utilization in Pakistan.," *Renew Sustain Energy*, pp. 1988–96, 2008.

[18] O. D. Mante, T. E. Amidon, A. Stipanovic, and S. P. Babu, "Journal of Analytical and Applied Pyrolysis Integration of biomass pretreatment with fast pyrolysis : An evaluation of electron beam (EB) irradiation and hot-water extraction (HWE)," *J. Anal. Appl. Pyrolysis*, vol. 110, pp. 44–54, 2014.

[19] C. Li *et al.*, "Bioresource Technology Comparison of dilute acid and ionic liquid pretreatment of switchgrass : Biomass recalcitrance , delignification and enzymatic saccharification," *Bioresour. Technol.*, vol. 101, pp. 4900–4906, 2010.

[20] A. Brandt, M. J. Ray, T. Q. To, D. J. Leak, J. Murphy, and T. Welton, "Green Chemistry Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid – water mixtures," pp. 2489–2499, 2011.

[21] M. Lynd, L.R., Laser, M.S., Bransby, D., Dale, B.E., Davison, B., Hamilton, R., Himmel and W. Keller, M., McMillar, J.D., Sheehan, J., " How biotech can transform biofuels.," *Nat. Biotechnol.*, pp. 169–172, 2008.

[22] A. J. Hallac, B.B., Sannigrahi, P., Pu, Y., Ray, M., Murphy, R.J., Ragauskas, "Effect of ethanol organosolv pretreatment on enzymatic hydrolysis ofBuddleja davidii stem biomass.," *Ind. Eng. Chem.*, pp. 1467–1472, 2010.

[23] K. Shill, S. Padmanabhan, Q. Xin, J. M. Prausnitz, D. S. Clark, and H. W. Blanch, "Ionic Liquid Pretreatment of Cellulosic Biomass : Enzymatic Hydrolysis and Ionic Liquid Recycle," vol. 108, pp. 511–520, 2011.

[24] F. Sun and H. Chen, "Evaluation of enzymatic hydrolysis of wheat straw pretreated by atmospheric glycerol autocatalysis," vol. 1044, April, pp. 1039–1044, 2007.

[25] F. Fuelbiol *et al.*, "Bioresource Technology The impact of glycerol organosolv pretreatment on the chemistry and enzymatic hydrolyzability of wheat straw," *Bioresour. Technol.*, vol. 187, pp. 354–361, 2015.

[26] F. Sun and H. Chen, "Enhanced enzymatic hydrolysis of wheat straw by aqueous glycerol pretreatment," vol. 99, pp. 6156–6161, 2008.

[27] D. Zhao, X.; Cheng, K.; Liu, "Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis.," *Appl. Microbiol. Biotechnol.*, vol. 82, pp. 815−827, 2009.

[28] A. A. D. S. Novo, L. P.; Gurgel, L. V. A.; Marabezi, K.; Curvelo, "Delignification of sugarcane bagasse using glycerol-water mixtures to produce pulps for saccharification.," *Bioresour. Technol.*, vol. 102, pp. 10040−10046, 2011.

[29] A. Roman, A. Ruiz, F. B. Pereira, and J. A. Teixeira, "Fractionation of Eucalyptus globulus Wood by Glycerol − Water Pretreatment : Optimization and Modeling," 2013.

[30] D. Vamvuka, S. Troulinos, and E. Kastanaki, "The effect of mineral matter on the physical and chemical activation of low rank coal and biomass materials," vol. 85,

pp. 1763–1771, 2006.

[31]　M. G. Montiano and C. Barriocanal, "Kinetics of Co-Pyrolysis of Sawdust, Coal and Tar," *Bioresour. Technol.*, 2016.

[32]　E. Popova *et al.*, "Bioresource Technology Thermal degradations of wood biofuels , coals and hydrolysis lignin from the Russian Federation : Experiments and modeling," *Bioresour. Technol.*, vol. 218, pp. 1046–1054, 2016.

[33]　Z. Gao, M. Zheng, D. Zhang, and W. Zhang, "Low temperature pyrolysis properties and kinetics of non-coking coal in Chinese western coals," *J. Energy Inst.*, vol. 89, pp. 544–559, 2016.

[34]　A. K. G. I.I. Ahmed, "Experiments and stochastic simulations of lignite coal during pyrolysis and gasification.," *Appl. Energy 102*, pp. 355–363, 2013.

[35]　 et al. No L.C. Bradley, S.F. Miller, B.G. Miller, "A study on the relationship between fuel composition and pyrolysis kinetics," *Energy Fuel 25*, pp. 1989–1995, 2011.

[36]　A. Ashraf, H. Sattar, and S. Munir, "Thermal decomposition study and pyrolysis kinetics of coal and agricultural residues under non-isothermal conditions," *Fuel*, vol. 235, pp. 504–514, 2018.

[37]　S. Oza, H. Ning, I. Ferguson, and N. Lu, "Composites : Part B Effect of surface treatment on thermal stability of the hemp-PLA composites : Correlation of activation energy with thermal degradation," vol. 67, pp. 227–232, 2014.