

KINETIC STUDY OF RICE BRAN BY **THERMOGRAVIMETRIC ANALYSIS**

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In

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CERTIFICATE

This is to certify that the project entitled, “**KINETIC STUDY OF RICE BRAN BY THERMOGRAVIMETRIC ANALYSIS**” submitted by **Sanjay Kumar Meher** is an authentic work carried out by him under my supervision and guidance for the partial fulfillment of the requirements for the award of **Bachelor of Technology (B. Tech) Degree in Chemical Engineering** at **National Institute of Technology, Rourkela**.

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Abbreviations

E_A =Activation Energy

TGA = Thermogravimetric Analysis

DTG = Differential thermogravimetry

H-C = Hydrocarbon

ABSTRACT

The rise of demand for fossil fuel keeps on reaching sky-high in the 21st century while the supply for it is diminishing day by day. It increased the quest to come up with an alternative source of fuel which can supply the rising demand. Biomass has the potential to cover up for the demands of needing alternate fuels. Biomass can be used as fuels directly by combustion process or by converting the biomass into fluid products. In this work, by using thermogravimetric analysis, the kinetic parameters (E_A =Activation energy) of rice bran at different temperatures and conditions has been determined. The activation energy of the rice bran was found out to be in lower range. It allows to blend rice bran into materials which has high activation energy and making pyrolysis feasible.

CHAPTER 1

INTRODUCTION

A biofuel is Hydrocarbon(HC) that made by or from living organic entity used as a source of energy. Any HC fuel delivered from natural matter (once alive material) in the brief time (day, week or month) considered as biofuel [24].

By distinctive procedures like natural, thermal and physical methods biofuel can be changed over in numerous energy forms. Fossil fuels have become limited, and the energy need increase day by day. The increment in the discharges rates of greenhouse gasses released from the utilization of these fossil presents at risk to the world atmosphere. Because of this, there is an urgent need to develop an alternative energy source that is energies efficient and economical. Pollution gives a significant motivating force to create bioenergy. The biofuel produced from biomass can be a substitute for fossil fuel. Biomass can contribute energy to world for consumption [21].

1.1.Current energy consumption

For developing countries, energy is an essential requirement. And the requirement is increasing so it need a huge investment

Based on different criteria energy can be classified into different types:

- A. Commercial energy and Non-commercial energy
- B. Primary energy and Secondary energy
- C. Renewable energy and Non-Renewable Energy

1.1.1. Primary energy and secondary energy

Primary energy is that form of energy that is available in the earth crust. It is directly, or by treatment could be utilized for heat production or mechanical work. For example coal, petrol, diesel. Secondary energy is that which was generated from other forms of energy.

1.1.2. Commercial & Non-commercial energy

The commercial energy is the form of energy that are directly available in the market for a definite price. For example- electricity, petrol, etc. and non-commercial energy are those which are not available in the commercial market like wood, cattle dunk.

1.1.3. Renewable energy and Non-Renewable Energy

The energy generated from natural resources like the wind, water are called as renewable energy. Example: hydroelectricity, geothermal power, wind energy and solar energy. And the non-renewable energy is those which are limited available in nature like fossil fuel and coal [19].

These days, the whole world almost either run on fossil fuels or employs it as a source for generating the energy. The most important groundbreaking steps for the rapid development of the 20th century is the utilization of fossils fuels up to the most. The chart represents the supply of global energy from different sources.

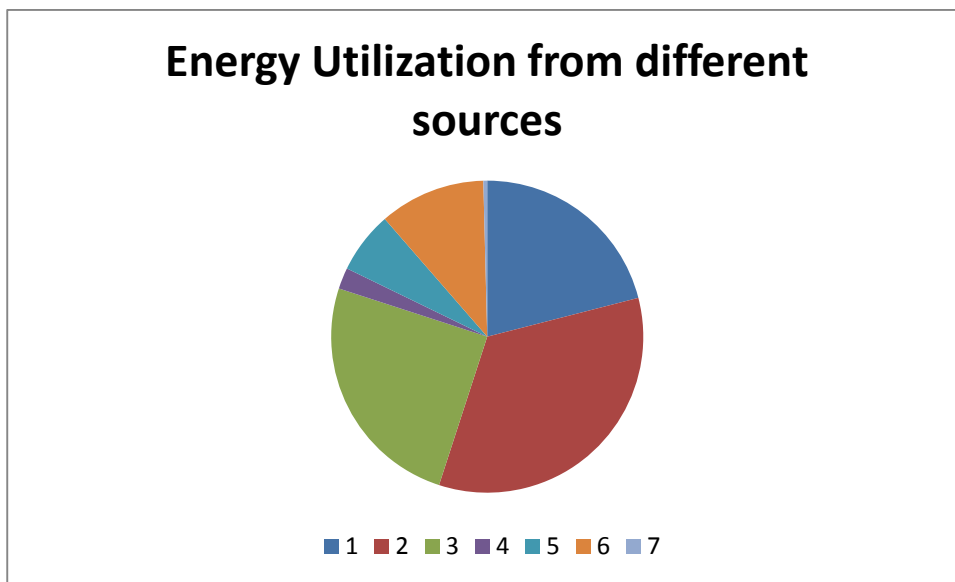


Figure 1.1. Total world energy supply by source

1. Natural gas
2. Oil
3. Coal
4. Nuclear plant power
5. Hydroelectric power
6. Biomass energy
7. Other sources of energy

1.2. PROBLEMS WITH FOSSIL FUELS

Fossil energies as the name mentions are subordinates of plant and creature fossils that are million of years of age. They are formed from the remains of the decayed plants and animals of the Carboniferous period. The three fuel sources coal, natural gas and oil/petroleum helps

to meet the energy and electricity demands of today's world. The three energy sources natural gas, coal, and oil/petroleum serve to meet the power and energy demand of today's world. The demand never decreases for the energy.

1.2.1 Disadvantages of Fossil Fuels

Global warming: Burning of fossil fuel produce carbon dioxide that causes air pollution. It is also a greenhouse gas that is the probable causes for world wide global warming issue.

Rising Prices: Many country mainly middle west countries have a large storage of fossil fuel and for the supply of fuel many countries depend on them. So the worldwide price of the fossil fuel is increasing.

Acid Rain: Vehicles & factories all burn fuel and when fuel burns polluted gas produce. Some gas like nitrogen oxide and Sulfur dioxide reacted with cloud water drop and converted nitric acid and sulphuric acid. Rain from this cloud is cause acid rain.

Non-Renewable: As the fossil fuels removed to a boundless & unrestricted level it is without a doubt that they will drain some time or another or the other. Though they are nonrenewable, it is likely that energizes costs will confront a series of treks in not so distant future. It would take a large number of years to replenish coal underground storage and oil reserve, and we are without any hesitation utilizing them very rapidly [16].

Coal Mining: Extraction of derivatives of coal from zones that have huge coal lumps stores is a fatal, risky & troublesome assignment as well as stance wellbeing risk to the lives of a many laborers who work in the coal mines. The coal extraction business crushes wide territories of areas and results in biological imbalance [3].

Need Huge Amount of Reserves: The coal utilizing plants needs immense and very large supply of derivatives of coal to create an expansive measure of power on a steady sustenance. This implies they need stores of coal practically prepare heaps of fuel close power stations to do the procedure of producing power. This is needed since today likewise numerous countries are reliant on coal as a noteworthy wellspring of creating force.

1.2.2 Rice Bran

Rice bran also called as Miller's Bran. It is the hardened outer layer covering the grain. It is considered to be an important part of the grain, and it was obtained during the milling process

of the grain. A portion of nutritional value is lost when it was removed from outside of the rice bran. Rice bran should not be confused with chaffs. Chaffs are coarser scaly type of material protecting the grain from outside. The high oil content makes bran subject to rancidification. This was the reason; it is separated from the grain before putting it into the storage.

It is a by-product of the milling process. It was obtained during the conversion of brown rice to white rice. It is rich in various antioxidants that have benefits for the human health. Rice bran contains 12 to 13 % oil and highly unsaponifiable components (4.3%) & it also contains many dietary fibers like beta-glucan, pectin and gum. Some research suggested that it contains some level of carcinogenic materials like arsenic.

CHAPTER 2

Literature Review

2.1. BIOMASS

Biomass alludes to many regular materials that are obtained or abstracted from any living organic entity it may be plants, or it might be any animals, i.e., vertebrates or invertebrates. Generally speaking, it is difficult to find the genuine definition. Biomass is not only non-fossilized but also normal biodegradable material beginning from living organisms, plants, animals and scaled down scale natural elements. This makes the things, symptoms, misuses & stores from cultivation, officer administration, common & cutting edge wastes. Biomass in like manner joins gasses and liquids recovered from the disintegration of biodegradable normal & nonfossilized materials.

The biomass we use for fuel incorporates wood, wood waste, straw, excrement, sugar stick, and numerous other by items from a mixed bag of farming procedures. At the point when smoldered, the concoction vitality is discharged as warmth. On the off chance that you have a chimney, the wood you smolder in it is a biomass fuel. What we now call biomass was the boss wellspring of warming homes and different structures for a large number of years. At the point when blazed, biomass does discharge carbon dioxide (CO₂), a nursery gas. Be that as it may, when biomass harvests were grown, a comparable measure of carbon dioxide is expanded through photosynthesis.

Ethanol, another biomass fuel, is a liquor refined basically from corn. For the last a quarter century, it has been mixed with gas for utilization in automobiles in the USA. Utilizing ethanol as a part of gas means we don't blaze as much fossil fuel in our automobile. Truly the pieces of the corn have been utilized to create ethanol. At the National Renewable Energy Laboratory, (NREL) in Golden CO. scientists are discovering approaches to turn whatever remains of the corn plant (corn stover) into ethanol.

Biomass is utilized as a part of a spot of coal in numerous force plants. The biomass is smoldered in the heaters to warmth water and produces steam to turn a turbine. The results of blazing are CO₂ and powder. New biomass harvests being planted to keep up the supply utilize the CO₂. The fiery remains are sent to farmers to use as compost.

2.1.1. SOURCES OF BIOMASS

The general wellsprings of biomass are natural, civil, woods & agrarian.

The samples of sources were examined below:

- Agricultural: sustenance grain, bagasse (pounded sugarcane), rice wheat, seed bodies, corn stalks, nutshells, straw, & excrement from dairy cattle, hogs & poultry.
- Forest: trees bark or wood, sawdust, wood waste, timber cut, & plant scrap.
- Municipal: Sewage slop, yard clippings, waste paper, & food waste.

It also includes coral reefs from beneath of the ocean.

- Biological: creature waste & natural waste.
- Excreta from animals, flying creature, people Furthermore from the animals of the profound oceanic zone.

2.2. BIO OIL

Bio oil, as it is known from its name, is obtained from biological organisms either it may be plants or it may be animals. 80% of the bio-oil should be renewable. All types of bio-oil are obtained as a product from photosynthesis process so indirectly it can be referred as a source of solar energy. The term biofuel implies as biomass fuel (i.e. in the form of solid liquid and gas). Solid biofuel includes: wood, sawdust, dried grass-bundles, household twigs and rags, charcoal, agricultural wastage, non-food energy crops and dried manure cakes where biodiesel, bio-alcohol, bio-ether, pyrolytic oil are liquid bio-fuel and syngas and biogas are gaseous biofuel.

2.3. BIOMASS CONVERSION PROCESS:

Biomass is, in general, converted to useful products mainly by two processes:

1. Thermo-chemical process.
2. Bio-chemical processes.

2.3.1 THERMOCHEMICAL PROCESS:

The thermo-chemical process includes mainly process like

1. Torrefaction
2. Liquefaction °C

3. Gasification

4. Combustion

5. Pyrolysis

2.3.1.1 Torrefaction

Torrefaction is a process of subjecting a biomass to a maximum temperature of 300 C in an idle and diminishing conditions. In some conditions, it is also forced to an environment of 200 °C to 280 °C. Again we can say that it is a gentle pyrolysis process based on lower temperature advent. After being the completion of this torrefaction process solid samples of unchanging with higher volatility content and lower water content was achieved. Many volatiles and ash containing elements ended up with higher temperature value and diminishing mass.

Torrefaction of biomass, e.g., wood or grain, is a gentle type of pyrolysis at temperatures normally somewhere around 200 °C and 320 °C. Torrefaction changes biomass properties to give a vastly improved fuel quality for burning and gasification applications. Torrefaction prompts a dry item with no natural action like spoiling. Torrefaction consolidated with densification prompts an extremely vitality thick fuel transporter of 20 to 21 GJ/tons lower warming worth (LHV). Torrefaction makes the material experience Maillard responses.

Biomass can be a critical vitality source. Then again, nature gives a huge assorted quality of biomass with fluctuating attributes. To make very productive biomatter-to-vitality chains, torrefaction of the biomass in mix with densification (pelletization or briquetting) is a promising stride to overcome logistic, financial aspects in vast scale feasible vitality arrangements, i.e. make it simpler to transport and store it. Pellets or briquettes are lighter, drier and stable away instead of the biomass they are made of. Torrefaction is a thermochemical treatment of biomass at 200°C to 320 °C. It is done under the barometrical weight and without oxygen, i.e. with no air. Amid the torrefaction prepare, the water contained in the biomass and, in addition, pointless volatiles are discharged, and the biopolymers (cellulose, hemicellulose, and lignin) somewhat decay, emitting different sorts of volatiles. The last item is the staying strong, dry, darkened material that is alluded to as torrefied biomass or bio-coal.

Amid the procedure, the biomatter regularly loses 20% of its mass (dry bone premise) and 10% of its warming quality, with no calculable change in volume. This volatility (the volatiles) was utilized as a warming fuel for the torrefaction process. After the biomass is torrefied, it can easily be densified, and rule into briquettes or pellets utilizing ordinary densification gear, to expand its mass and vitality thickness and to enhance its hydrophobic properties. The historical backdrop of torrefaction retreated to the start of the 19th century and utilized in large scale during the 2nd World War

2.3.1.1.1 Market for Torrefied Biomass

Torrefied biomatter and biomass have included quality for distinctive markets. Biomass when all is said in done gives a minimal effort, okay course to lower CO₂-outflows. At the point when high volumes or amounts were required, torrefaction can make biomass from removed sources cost focused due to denser material simpler to store and transport.

Wood powder fuel:

- Torrefied wood powder were ground into a fine powder and when packed, imitates melted petroleum gas (LPG).

Vast scale co-terminating in coal-let go force plants:

- Torrefied biomass brings about lower taking care of expenses;
- Torrefied bio matter empowers higher co-terminating rates;
- Product was conveyed in a scope of LHVs (20–25 GJ/ton) and sizes (briquette, pellet).
- Co-terminating torrefied biomass with coal prompts lessening in net force plant emanations. Steel creation:
- Fibrous biomass is extremely hard to convey in heaters;
- To supplement infusion coal, biomass item needs to have LHV of more than 25 GJ/ton. Private/decentralized warming:
- Relatively high rate of transport on wheels in the store network makes biomass extravagant. Expanding volumetric vitality thickness does abatement costs;

- Limited/congested storage room builds requirement for expanded volumetric thickness/expansion;
- Moisture/water content vital as dampness prompts smoke and smell.

Biomass-to-Liquids:

- Torrefied biomatter and biomass bring about less taking care of expenses;

2.3.1.2. Liquefaction

The conversion process of biomass material transforming it into a usable biofuel or any helpful chemical product accompanied by the help of a useful catalyst or by an intriguing solvent is defined as liquefaction. This process is carried out at a temp. Of 350°C accompanied by a pressure of about 12 to 20 MPa. Different solvents like Glycerol, Phenol and even water in some hydrogenic and nitrogenic atmosphere. Even sometimes alkalis also help in the upgradation organic process. The main or the primary product is an organic liquid with diminished O₂ content. The properties and the nature of these products primarily depend on the type of catalyst used rather than the physical and chemical conditions they were undergone.

Liquefaction is a term utilized as a part of materials sciences to allude to any procedure that either produces a fluid from a strong or a gas or creates a non-fluid stage that acts as per liquid dynamics. Liquefaction happens both as a significant aspect of regular procedures, and in man-made procedures utilized as a part of science and trade. For instance, " real business utilization of liquefaction is the liquefaction of air to permit partition of the constituents, for example, oxygen, nitrogen, and the honorable gases", while another application is the transformation of strong coal into a fluid structure usable as a substitute for fluid energizes. In material science and science, the stage moves from strong, and gas to fluid (softening and build up, individually) were alluded to as liquefaction. The liquefying point (here and there called liquefaction point) is the temperature and weight at which a strong turns into a fluid.

In business and mechanical circumstances, the procedure of consolidating a gas to the fluid is infrequently alluded to as liquefaction of gasses.

2.3.1.2.1 Coal Liquefaction

- Coal liquefaction is a procedure of changing over coal into fluid hydrocarbons: fluid powers and petrochemicals. The transformation business was usually alluded to as "coal change" or "Coal to X". "Coal to Liquid Fuels" is typically called "CTL" or "coal liquefaction." Despite the fact that "liquefaction" is for the most part utilized for a non-synthetic procedure of getting to be fluid. Today, the offer of changed over coal used for CTL is under 50%. It would diminish drastically in the following years with the improvement of "coal to chemicals" and "coal to SNG" units, chiefly in China.
- **Direct processes**
- **Indirect Processes**

Particular liquefaction advances generally fall into two classifications: direct (DCL) and circuitous liquefaction (ICL) forms. Liquefaction forms for the most parts include gasification of coal to a blend of CO and H₂ (syn gas). Fischer–Tropsch process to change over the syn gas blend into fluid hydrocarbons. By difference, direct liquefaction procedures proselyte coal into fluids specifically, without the moderate stride of gasification, by separating its natural structure with the utilization of solvents or impetuses in a more weight and temperature environment. Since fluid hydrocarbons generally have a higher hydrogen-carbon molar proportion than coals, either by hydrogenating or by carbon-dismissal procedures should utilized in both ICL and DCL advancements.

As coal liquefaction by and large is a high-temperature/high-weight processes. It obliges a noteworthy vitality utilization and at mechanical scales (a huge number of barrels of gallons per day), and a multi-billion dollar capital speculations. Accordingly, coal liquefaction is just financially reasonable at verifiably high oil costs, and in this way displays a high venture hazard.

Backhanded coal liquefaction (ICL) procedures work in two stages. In the first stage, coal is changed over into syngas (a cleansed blend of CO and H₂ gas). In the second stage, the syngas is changed over into light hydrocarbons utilizing one of three fundamental procedures: Fischer-Tropsch combination, Methanol union with resulting transformation to gasoline or petrochemicals, and methanation.

Fischer-Tropsch is the most seasoned of the ICL forms. It was initially utilized on the extensive specialized scale as a part of Germany somewhere around 1934 and 1945 and is right now being used by Sasol as a part of South Africa (see Secunda CTL).

In methanol combination forms, syn gas is changed over to methanol, which is therefore polymerized into alkanes more than a zeolite impetus. This procedure, under the monitor ("Methanol To Gasoline") or the MTG, was created by Mobil in the midst of 1970s, and is being tried at a showing plant by Jincheng Anthracite Mining Group (JAMG) in Shanxi, China. Taking into account this methanol amalgamation, China has likewise added to an in number coal-to-chemicals industry, having yields, for example, olefins, MEG, DME, and aromatics.

Methanation response changes over syngas to substitute normal gas (SNG). The Great Plains Gasification Plant in Beulah, North Dakota is a coal-to-SNG office creating 160 million cubic feet for every day of SNG and has been in operation since 1984. A few coal-to-SNG plants are in operation or venture in China, South Korea, and India.

The above occurrences of business plants in view of circuitous coal liquefaction forms and in addition numerous others not recorded here incorporating those in arranging stages and under development, are arranged in the Gasification Technologies Council of World's Gasification Databases.

2.3.1.2.2 Environmental Consideration

Most coal liquefaction procedures were connected with critical CO₂ outflows from the gasification process from the warmth and power inputs to the reactors, subsequently adding to an unnatural weather change, particularly if coal liquefaction was directed without carbon catch and capacity technologies. High - water utilization in the water-gas movement or methane steam varying responses is another unfavourable natural impact. Then again, engineered energies created by backhanded coal liquefaction procedures have a tendency to be "cleaner" than generally happening crudes, as heteroatom (e.g. sulfur) mixes are not integrated or were avoided from the last item. Pyrolysis of coal produces polycyclic fragrant hydrocarbons, which are known cancer-causing agents

CO₂ outflow control at Erdos CTL, an Inner Mongolian plant with a carbon catch & capacity show task, includes infusing CO₂ into the saline aquifer of Erdos Basin, at a rate of 100,000

tons for every year. Starting late October 2013, a gathered measure of 154,000 tons of CO₂ had been infused subsequent to 2010, which came to or surpassed the configuration value. [

At last, coal liquefaction-inferred fills will be judged in respect to targets set up for low-nursery gas discharges fuels. [for instance, in the US, the Renewable/ recyclable Fuel Standard and Low-carbon fuel standard, for example, sanctioned in the State of California mirror an expanding interest for low carbon foot shaped impression energizes. Likewise, enactment in the United States has confined the military's utilization of optional fluid fills to to have life-cycle GHG emanations not exactly or equivalent to those of their customary petroleum-based proportional, as needed by Section 526 of the Energy Scrutiny Independence and Security Act (EISA) of 2007

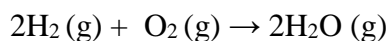
2.3.1.3. Combustion

Combustion as the word defines itself, a complex reaction combustible in nature realizing the fair amount of heat energy and light energy and seldom accompanied by the sound and various energy. This reaction is exothermic in nature realizing heat energy. When biomass is subjected as fuel the oxidation reaction that takes place during combustion results in the formation of carbon, CO₂, sulfur, compounds containing various gasses. The combustible reaction is seldom also called as ignition reaction [12]. The glowing process reports in as gas stage response and surface response or even sometimes both.

Different examples of this are diffusion, evaporation, convection, radiation heat conduction, and high luminescence. Some complex reaction is even accompanied by advanced, complicated very high velocity. The gaseous fuel obtained from different sources burns straight forward in a gaseous phase. Similarly, liquid fuels also burns in the gaseous stage after surface vanishing this may be regarded as evaporation burning. Many some heavy oils or oil with high complexity burns in this manner i.e. evaporation burning. The disintegration or braking down into smaller parts generates a large amount of heat.

Burning or Combustion is a high-temperature exothermic reaction redox synthetic response between a fuel and an oxidant, generally environmental oxygen, which creates oxidized, frequently vaporous items, in a blend termed as smoke. Ignition in a flame creates a fire. Also, the warmth delivered can make ignition self-managing. Burning is regularly a muddled arrangement of basic radical responses. Strong fills, for example, wood, first experience endothermic pyrolysis to deliver vaporous powers whose ignition then supplies the warmth

needed to create a greater amount of them [14]. Burning is regularly sufficiently hot that light as either sparkling or a fire is created. A basic case can be found in the ignition of H₂ and O₂ into the H₂ (gas) water vapor, a response ordinarily used to fuel the rocket motors. That response discharges 242 kJ/mol of enthalpy (warmth):



Uncatalyzed burning in the air requires genuinely high temperatures. Complete burning is stoichiometric regarding the fuel, where there is no remaining fuel, and preferably, no staying oxidant. Thermodynamically, the synthetic balance of burning in air is overwhelming as an afterthought of the items. Be that as it may, finish burning is verging on difficult to accomplish, following the substance balance is not so much come to, or may contain unburnt items, for example, CO, (H₂) hydrogen and even carbon (residue or cinder). Accordingly, the delivered smoke is poisonous and contains unburnt or incompletely oxidized items.

Any ignition at high temperatures in air, which is 78 percent nitrogen, will likewise make little measures of a few nitrogen oxides, ordinarily alluded to as NO_x, since the burning of nitrogen is thermodynamically supported at high, however not low temperatures. Since burning is seldom clean, vent gas cleaning or exhaust systems may be needed by law.

Flames happen actually, touched off by lightning strikes or by volcanic items. Burning (flame) was the initially controlled compound response found by people, as pit fires and blazes and keeps on being the principle technique to create vitality for mankind. Normally, the fuel is carbon, hydrocarbons or more convoluted blends, for example, wood that contains halfway oxidized hydrocarbons. The warm vitality created from burning of either fossil energizes, for example, coal or oil or from renewable or recyclable fills, for example, kindling, is gathered for various uses, for example, cooking, generation of power or modern or residential warming. Burning is likewise presently the main response used to power rockets. Burning is likewise used to pulverize (burn) waste, both non-hazardous and perilous.

Oxidants for burning have high oxidation potential and incorporate environmental or unadulterated oxygen, chlorine, fluorine, chlorine trifluoride, nitrous oxide and nitric corrosive. Case in point, hydrogen smolders in chlorine to shape hydrogen chloride have the freedom of warmth and light normal for burning. Albeit generally not catalyzed, burning can be catalyzed by platinum or vanadium, as by the help contact process.

2.3.1.3.1 Types of Combustion

Complete Combustion

In the complete ignition, the present reactants smolder in (O_2) oxygen, creating a set number of items. At the point when a hydrocarbon smolders in oxygen, the response will yield carbon dioxide and water. At the point when components are smoldered, the items are essentially the most well-known oxides. Carbon will yield carbon dioxide, sulfur will yield sulfur dioxide, and iron will yield iron (III) oxide. Nitrogen is not thought to be a flammable substance when oxygen is the oxidant, yet little measures of different nitrogen oxides (usually assigned NO_x species) structure when air is the oxidant. Combustion is not so much ideal to the greatest level of oxidation, and it can be temperature-subordinate.

For instance, sulfur trioxide is not created quantitatively by the burning of sulfur. NO_x species show up in huge sums above around $2,800\text{ }^\circ\text{F}$ ($1,540\text{ }^\circ\text{C}$), and more is delivered at higher temperatures. The measure of NO_x is likewise an element of oxygen excess. In most mechanical applications and flames, air is the wellspring of oxygen (O)

2) In the air, every mole of oxygen is blended with roughly 3.71 mol of nitrogen. Nitrogen does not join in ignition, but rather at high temperatures some nitrogen will be changed over to NO (For the most part NO, with much littler measures of NO_2). Then again, when there is inadequate oxygen (O_2) to totally combusted the fuel, some carbon fuel is changed over to carbon monoxide (CO) and a portion of the hydrogen (H_2) stays un-reacted. A more finish set of mathematical statements for the burning of an HC in the air hence requires an extra computation for the conveyance of O_2 between the carbon (C) and (H) hydrogen in the fuel. The measure of air needed for complete ignition to occur is known as hypothetical air. In any case, practically speaking the air utilized is 2-3x that of hypothetical air.

Incomplete Combustion

Fragmented ignition will happen when there is insufficient O_2 to permit the fuel to respond totally to deliver CO_2 and H_2O . It likewise happens when the ignition is extinguished by a warmth sink, for example, a strong surface or fire trap.

For most energizes, for example, diesel oil, coal or wood, pyrolysis happens before burning. In inadequate burning, results of pyrolysis remain unburnt and pollute the smoke with toxic particulate matter and gasses. Mostly oxidized mixes are likewise a worry; incomplete

oxidation of ethanol can deliver unsafe acetaldehyde, and carbon can create dangerous CO (carbon monoxide).

The nature of ignition can be enhanced by the outlines of burning gadgets, for example, burners and inside ignition motors. Further upgrades are achievable by synergist subsequent to blazing gadgets, (for example, exhaust systems) or by the straightforward fractional return of the fumes gasses into the ignition process. Such gadgets are needed by natural enactment for autos in many nations, and may be important to empower expansive burning gadgets, for example, warm power plant stations, to achieve or reach the lawful emanation measures.

The level of ignition can be calculated or measured and broke down with test hardware. HVAC builders, fire fighters & designers use ignition tester or analysers to test the proficiency of a copier amid the burning procedure [15]. Furthermore, the effectiveness of an interior ignition motor can be measured in this way, and some U.S. states and neighbourhood districts use burning investigation to characterize and rate the effectiveness of vehicles out and about today.

Smouldering

Smouldering is the moderate, low-temperature, flameless type of ignition, maintained by the warmth advanced when oxygen straightforwardly assaults the surface of a dense stage fuel [21]. It is an ordinarily inadequate ignition response. Strong materials that can manage a seething response incorporate coal, cellulose, wood, cotton, tobacco, peat, duff, humus, manufactured froths, roasting polymers (counting polyurethane froth) and dust. Regular samples of seething phenomena are the start of private flames on upholstered furniture by powerless warmth sources (e.g., a cigarette, a shortcircuited wire) and the industrious burning of biomass behind the flaring fronts of fierce blazes.

Rapid

Quick burning is a type of ignition, also called a flame, in which a lot of warmth and light vitality are discharged, which frequently brings about a fire. This is utilized as a part of a type of hardware, for example, interior burning motors and in thermobaric weapons. Such an ignition is often called a blast, however for an inside burning motor this is wrong. An inside is burning motor ostensibly works on a controlled quick smolder. At the point when the fuel-air blend in an inside burning motor blasts, that is known as an explosion [18].

Spontaneous

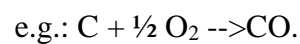
Spontaneous ignition is a kind of burning which happens without anyone else warming (increment in temperature because of exothermic interior responses), trailed by warm runaway (self-warming that quickly quickens to high temperatures) lastly, ignition. Case in point, phosphorus self-touches off at room temperature without the use of warmth.

Turbulent

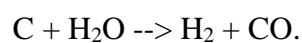
Ignition bringing about a turbulent fire is the most utilized for modern plant application (e.g. gas turbines, gas motors, and so on.) in light of the fact that the turbulence helps the blending process of the supplied fuel and given oxidizer..

2.3.1.4. Gasification

The process by which the carbon containing material are converted to vapourous fuels at high temperature is called as gasification. The yield that we get from heating varies from large ranges it is from about 1/10 to 50% of that of common gasses [7]. The gas that we get from this process is directly used motoring clean up and also in the direct terminating of the boiler. Also, it can be used for creating gasses like methanol and hydrogen for the fulfillment of the energy need. Though combustion is used widely still, gasification of bio matter has much more advantages on combustion over cleanliness and productiveness and also in the financial aspects. Durning gasification there employ some specific steps. The main purpose of it is to do pyrolysis and realizing all volatile content [16]. At the same time, carbonaceous matter is also released. For much further char is formed in the process and this unusable items reacts with oxygen to form CO₂ and CO, which releases temp. For much later in the gasification process.



In the last step of the gasification process, the CO₂ that is formed reacts with Steam & Char present in the system and releases H₂ and CO.



2.3.1.5. Pyrolysis

The process by which the biomass and biomatter decay in heat at normal temperature without the presence of oxygen is called as pyrolysis. During pyrolysis feedstock is subjected to the reactor, here heat is released by the other expansion of different operators like air, steam, O₂, H₂ post ignition and handling of the other gases, this create very critical and important step. Pyrolysis ingredients are largely comprised of gasses like methane ammonia and CO₂ similar to that of Bio oils ethanol acetones and acetic acid, etc. The output from this process heavily supported on process and system control and conditions, very acute temperature control, conditions of the biomass and its properties and nature, and also on the arrangement on that time being. Here in this process biomasses are heated up to high temperature and undergoes rapid cooling that gathers the desired fluid that is later designated as Bio fuel. It is carried out to suppress the diminishing and deteriorating state of the transition substance during pyrolysis. At this time when it is being cooled the volatiles gathers to form bio-oil. This is an exceptionally good main stream strategy, which makes the fair quantity of liquid fuel from the given sample bio mass. This becomes economical and easy to carry out for the transportation purposes. The negative and demerits facts about the pyrolysis of bio-oil is given as follows:

- The time gap for the biomass to get converted to secondary state is less than 2 seconds therefore everything should be carried out swiftly.
- The Bio Char, which is formed during the reaction, is potential threat to the remaining cracking reaction, so it must be removed in time to carry out the reaction.
- The vapor that is formed during the reaction of cracking must be cooled down quickly to get the best results out of it.
- To obtain the Bio Oil to get best value temperature should be maintained around 400°C - 500°C
- To get the best results out of it the biomass size should be well under 3mm.

2.3.2. BIO CHEMICAL PROCESS

This is described as the process that revolves around the bio chemical change of certain samples types such as different bio waste other bio matter, etc. It involves plants and industries based on certain biological matter conversion [13]. Some of the examples of such industries are paper industries and some vital organics producing industries like sugar

industries, rice mills, etc. It uses some vital, but efficient methods like enzymatic based activities, hydrolysis based methods, and some pre-treating methods or ways.

Other sorts of these biochemical ways consist of the Alcoholic maturation process and different types of anaerobic absorption processes. These earlier processes that are used uses deteriorating or breaking sample material into biogas which contains CO₂ and CH₄ as its composition without the presence of the oxygen. Due to its high calorific value content it is used as creating power energy that again helps in the alcoholic aging processes and also helps in the generation or production of different wines form variety of biomass like sugar crops and high starch containing different crops [12].

It can also be utilized in the production of different fuels by using some of the activity of different life forms like yeast which aides in the yielding of this amazing transporting fuels. During the process, it was advised to separate the long chains of polysaccharides by the variant process of hydrolysis. Later it can be simplified and refined and also can be used as an alternative of petrol because as it contain fair bits and amounts of ethanols containing compounds [14].

CHAPTER 3

MATERIALS AND METHODS

3.1 Raw material

The Rice bran sample that is used in this experiment was supplied from a rice mill of Sambalpur, Odisha, India. The rice bran sample was in lumped forms and was further powdered by the help of a grinder [1]. It is done to reduce the voids inside the reactor for better heat distribution. Rice bran is a by-product of the rice milling process (the conversion of brown rice to white rice), and it contains various antioxidants that impart beneficial effects on human health [5]. Rice bran also contains a high level of dietary fibers (beta-glucan, pectin, and gum). However, some research suggests there are levels of inorganic arsenic (a toxin and carcinogen) present in rice bran [9].

3.1.1 Characterization of Raw Materials

The rice bran was analysed to check the change and improve the different properties of the solid materials due to pyrolysis. The sample is brownish yellow in colour and amorphous in nature.

3.1.1.1 Proximate Analysis of Raw Materials

By the help of proximate analysis, we can get information about the different content of the sample. We can get moisture content, fixed - carbon content volatile matter content as well as ash content. It was done with the help of *ASTM D3172 - 07a* method.

Table 3.1 Proximate analysis of Rice Bran

Properties	(Wt. %)
Moisture content	6.7
Volatile content	85.1
Ash content	4.1
Fixed carbon	4.1

3.1.1.2 Ultimate Analysis of Raw Materials

The process by which it can determine or calculate/estimate the elemental composition of a given sample is known as Ultimate Analysis. It is done by the help of a CHNSO elemental

analyzer that gives the elemental composition of the sample. Carbon Sulphur Nitrogen Hydrogen percentage are determined by it. By subtracting these values from a total of 100 percent we can get the oxygen percentage.

Table 3.2 Ultimate analysis of Rice Bran

Ultimate analysis (wt%0	
C	64.986
H	9.942
N	3.583
S	0.227
O	21.262
C/H molar ratio	0.54
C/N molar ratio	21.23
Calorific Gross value (MJ/kg)	22.06

3.1.1.3 Calorific Value

It can be defined as the amount or quantity of heat generated when a 1 kilogram of the given material is burnt. It is done by the help of an instrument called as Bomb Calorimeter [10]. The **heat of combustion** (ΔH_c°) is the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions [19]. The chemical reaction is typically a hydrocarbon reacting with oxygen to form carbon dioxide, water, and heat.

3.1.1.4 Oil content

It is defined as the amount of oil present in a product as supplied to an end user. By using the Soxhlet apparatus, the oil content of a material is calculated.

3.1.1.4 .1 Soxhlet Apparatus

Soxhlet apparatus is designed for the lipid extraction from the solid materials. It is used only if the required compound has a limited solubility rate in the given solvent and also if the impurity or bogus is insoluble in the solvent. It can be used in the unmanaged and unmonitored activities or operations while allowing the efficient recycling of the small amount of solvent to dissolve in a large amount of materials [22]. It is made up of 3 main components. A percolator (boiler and reflux) which helps in the circulation of the solvent, a thimble (generally made out of thick filter like paper) which retains the solid to be laved, and a siphon mechanism which periodically empties the time.



Figure 3.2 Soxhlet Apparatus

3.2 Thermogravimetric Analysis

Pyrolysis is the process of heating a material/substance or, in this case, a sample at a definite temperature in the complete absence of the air. So for the better effectiveness of pyrolysis the acute temperature must be determined. That's the reason TGA of the sample was completed by the help of a DTG 60 machine. A precise amount of 20 mg to 30 mg of sample was subjected around a temperature of 800 °C. The resident time was considered to be only 1 Minute. It was performed at different heating rates at different atmospheric conditions. 25 °C /min in both air and N₂ medium and 20 °C /min in an air medium. Then the TGA mass loss curve was plotted versus the temperature. TGA supplies the range in which Maxim thermal degradation of the sample is taken place.



Figure 3.3 Thermogravimetric Analyser

CHAPTER 4

RESULTS & DISCUSSION

4.1 Characterization of rice bran

The simplest, quickest, and effective way of analyzing fuel quality is by doing the proximate analysis. The effective conversion efficiency is affected by the high moisture content because it affects the heating value of the sample biomass and has the tendency of deteriorate energy quality due to decomposition during the storage [8]. High ash content and high volatile content can also affect the heating value in a negative way. Due to higher volatile contents, the sample will exhibit more volatility than the solids fuels. The carbon content should not be less during the pyrolysis process [19]. As it contains 85.1% of volatile matter, the sample is a good alternative source of energy. Here the ash contents of the rice bran is 4.1%, so it will not pose any operational problems like disposal cost handling. Slagging and another processing cost. Table 3.2 shows the elemental composition of the given sample. It contains 64.9 % of carbon, 21.2% of O₂ which are suitable for the combustion process. The other elemental composition like Nitrogen = 3.58% , Sulphur = 0.22% and hydrogen is 9.9% that is very identical to many other types of biomasses. The calorific value of the rice bran is 22.06 MJ/kg that makes it a very potential candidate for an alternative fuel.

4.2 TGA and DTG analysis

Figure 4.1 shows TGA analysis plot at different heating rates of rice bran sample various atmospheric conditions i.e., Nitrogen and Air. The devolatilization is one of the characteristic parameters presented in this section. The rice bran TGA presents the active pyrolytic region or zone that exists in the temperature region of 235 °C and 490 °C. Here the evaporation of the moisture is represented in the first stage of decomposition. The formation of main volatiles like CO and CO₂ is indicated in the 2nd stage of decomposition. The residue which formed during the pyrolysis decomposed slowly. At this time, the weight loss velocity started to decrease, and the residue ratio came to a constant. At the end of the decomposition reaction of the hydrocarbon, a three-stage weight loss curve is obtained.

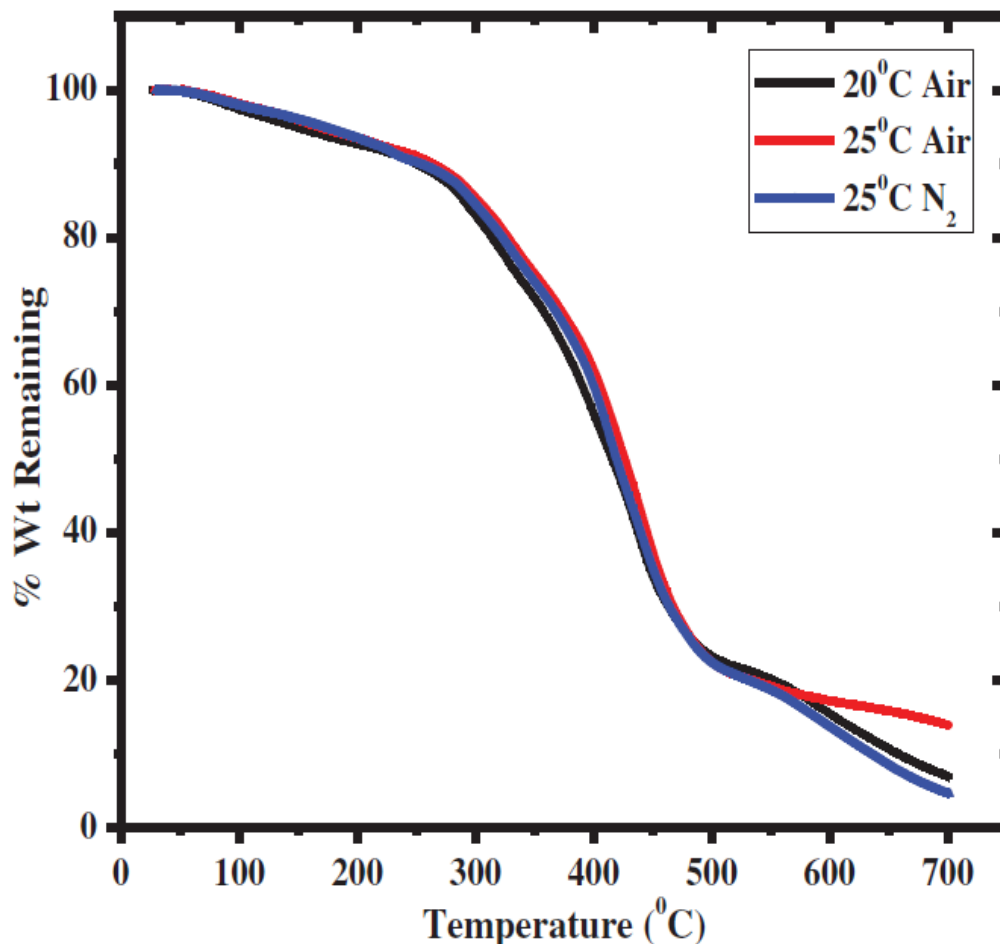


Figure 4.1 TGA curve of rice bran at different heating rates

5.1 % of weight loss was occurred during the early initiation of the decomposition due to the removal of moisture and water content in the Rice bran. 82.4% of weight loss occurs due to the release of volatile matter content, and the remaining 12.5 % are coined as char residue of the rice bran. Here in this case the secondary stage of disintegration or decomposition is coined as active pyrolytic zone due to rapid disintegrating or decomposing rate per unit time. In this second stage, the weaker bonds are destroyed, and the intermolecular interaction between them is also affected which results in breaking of those bond. Some of the gaseous molecules are formed due to the lower temperature, and some aliphatic side chains are also damaged. In the 3rd stage, the parent molecular skeleton and many chemical bonds are destroyed due to the presence of very high temperature. This accompanies the formation of smaller molecules because of the decomposition of the larger molecules. They appear in the

gaseous phase and even in char remains. The properties of the biomass change indifferently nitrogen atmosphere to that of air atmosphere.

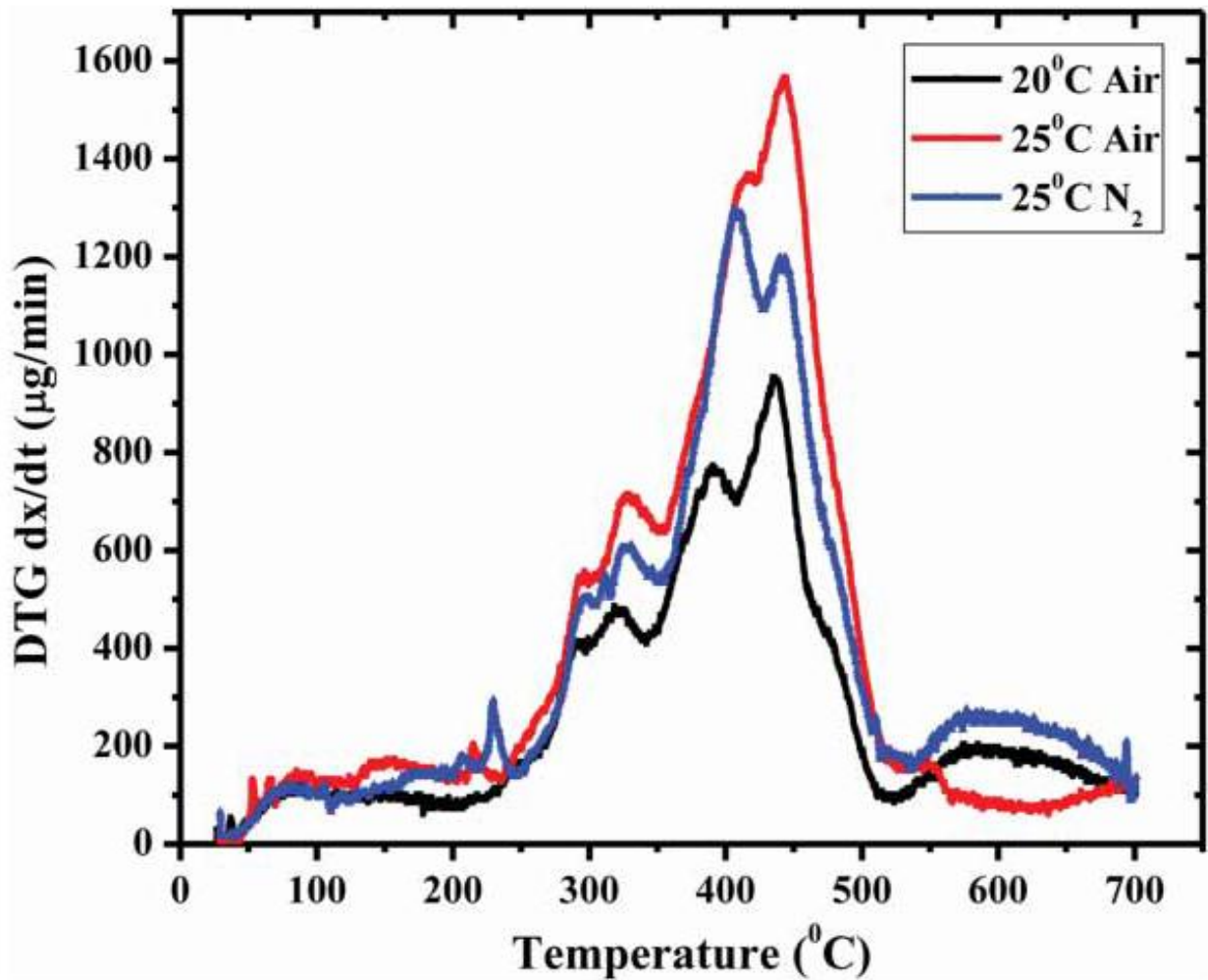


Figure 4.2 DTG curves for rice bran in different heating rates

In the above figure 4.2 the DTG curve for the rice bran sample predicts the normalised at loss rates for the supplied heating rates of 20°C /min and 25°C /min for the atmospheric air conditions and 25°C /min for the N₂ atmospheric condition. Biomass are composed mainly of three things cellulose,

Lignin and hemi-cellulose. The pyrolysis of these components provides us with two main peaks. At lower temperature, the first one attributes to the different heterogeneous oxidation and also to the pyrolysis.

The second one is corresponded to the char combustion. The component like hemi cellulose responds to the lower thermal stability that is why both the peaks are presents at the lowest temperature i.e. 230°C and 440°C. The cellulose which is present in the sample disintegrates

in a narrow peak of 320°C. And the peak that is wide and low is corresponded to the char combustion. At last lignin are volatilities in a very wide range of heating , results in the formation of high char yield in a temperature of about 560°C.

4.3 Kinetic Study by TGA

For the ease of an pyrolytic reactions it is necessary to determine the E_A of a given sample , and to determining the E_A we need to do the kinetic study of that given reaction. Figure 4.3 features the plot of $\ln(-\ln(1-x))$ versus $1/T$. Reactions with low activation energy occur easily rather than the reaction with higher E_A .

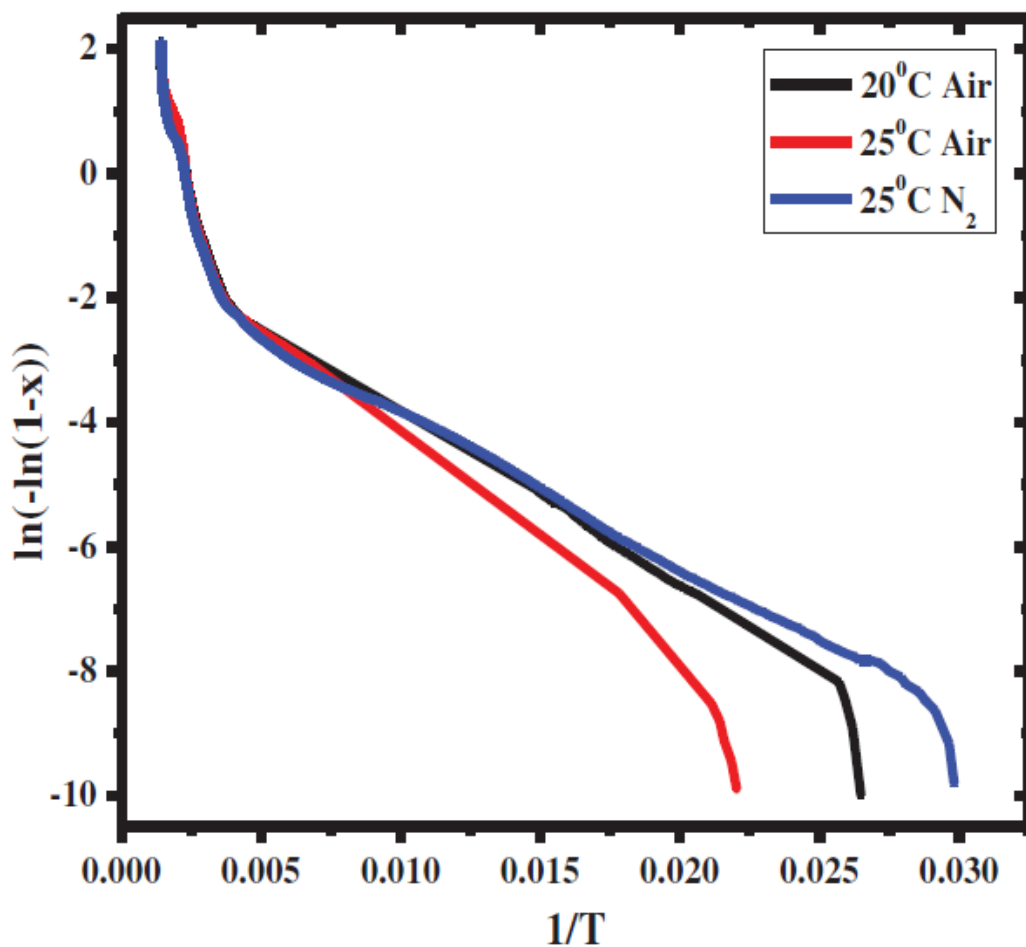


Figure 4.3 Kinetic analysis plot for determination of E_A

The reaction performances of biomass materials composed of lignocelluloses component can be determined by the kinetic reaction study. The E_A of three phases of disintegration due to

thermal pyrolysis is shown in Table 4.1. From this plots, we concluded that the degradation reaction of rice bran is based on the dependence of Arrhenius Equation.

Table 4.1 Activation Energy for pyrolysis of Rice Bran

Atmospheric Condition	Activation Energy (kJ/mol)		
	1 st Phase	2 nd Phase	3 rd Phase
N ₂ at 25 ^o C/ min	10.13	2.06	14.14
Air at 25 ^o C/min	14.26	2.85	15.09
Air at 20 ^o C/min	22.25	2.29	23.39

The active variation in E_A for rice bran suggests different thermal degradation due to variation in different chemical regimes.

- In the 1st phase, E_A of rice bran was 10.13kJ/mol, 14.26kJ/mol and 22.52 kJ/mol at different heating rate of 25^oC/min in N₂, 25^oC/min and 20^oC/min in air,
- In the second phase, the E_A of sample was 2.06kJ/mol, 2.58kJ/mol and 2.29 kJ/mol for the heating rates of 25^oC/min in N₂, 25^oC/min and 20^oC/min in air,
- In the 3rd phase, the E_A of sample was 14.14kJ/mol, 15.09kJ/mol and 23.4 kJ/mol for the different heating rates of 25^oC/min in N₂, 25^oC/min and 20^oC/min in air,

It was found that the kinetic parameters in the 2nd peak were greater than that of the 1st peak of the sample. The E_A of the sample is proportional to the frequency factor of the sample as it is stated in the Arrhenius equation. The air atmosphere has the highest activation energy value that represents the high temp. Sensitivity in the air medium. Besides this, it is also evident that the thermal disintegration or degradation of rice bran in air atmosphere may be affected by the mass and thermal transfer limits. Evidently it can easily said that E_A in air atmosphere was higher than that of the N₂ atmosphere.

CHAPTER 5

CONCLUSION & FUTURE WORK

5.1 CONCLUSION

We can interpret the physical as well as chemical characteristics and properties and also the thermal operational behavior of a particular supplied sample by the help of Thermogravimetric study. By determining different kinetic parameters, it will be helpful in designing more cost effective conversion processes and optimum pyrolysis techniques. The rice bran is comprised by low ash content and high volatile matter content, thus making it suitable and attractive for many thermochemical processes. At the temperature range of 235°C – 490°C, the highest degree of conversion & reaction is found out. The E_A in the N_2 atmosphere is lower than that of air atmosphere because of high-temp.

Sensitivity reaction in air atmosphere. This concludes a reminder that rice bran has the potential factor of getting converted into biofuels or might be get used as fuels for energy in the upcoming future.

5.2 Future work

- By the help of some different catalyst, we can produce a high yield.
- The oil has a good potential to eliminate the rising fuel demands in the century.
- The biomass can be blended with other materials with higher activation energy.

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