Slow Pyrolysis Mechanism and Kinetic Modeling of Scenedesmus Quadricauda Biomass

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DEDICATION

I would, in all my humility, dedicate this thesis work to my father Ghulam Sarwar Khan and mother. Heartfelt perseverance and devotion of all my mates and most unforgettably memorable, Mr. Zaheer Abbas Khan, being a cousin has been my subtle support throughout the master degree. As for the teachers, I find my words totally numb at this point to express my gratitude.

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With my solemn acknowledgement of all the ability and consistency to be only a mercy of Allah mighty, I utterly recall the blessings of my beloved prophet (PBUH)upon all my accomplishments.

Royally privileged must I be, that having by my side personalities as honorable as Dr. Salman Raza Naqvi, Dr. Taqi Mehran, Dr. Umair Sikandar and Dr. Asif Hussain Khoja, I am lamped to find my way all the while long. Had it not been for their kind and kindling considerations, I would never have found it done in the end. Having said that, the unflinching moral support as always been given by my family and friends shall always be my candle in the dark. And to all the employees and lab attendants goes my heartiest big Thank You!

Abstract

S. quadricuda’s bioenergy potential was studied via pyrolysis by the use of thermodynamic and kinetic analysis. Mean energies of activation which were calculated using isoconversional techniques were 152.370(±20.93O) and 153.000 (±21.23O) and 174.980 (±22.38O) Kj/mol, utilizing Friedman& Vyazovkin’s advanced techniques and OFW technique. From joined analysis it was known that A1/4 reaction model of Avrami-Erofeev was most likely a single step reaction mechanism. But according to profile of activation energy there was complicated degradation in active pyrolysis zone, in this zone there were independent two parallel reactions. Fot the conversion at low temperature mean energy of activation was 77.950 (±3.12o) kJ/mol with 4.860E4 (±2.240E4) 1/s pre-exponential factor and $n = 1.510\ (\pm 0.100)$, And high temperature 73.26 0(±17.93O) kJ/mol mean activation energy is recorded. Whereas pre-exponential factor was 1.320E03 (±2.610E3) s-1, and n=1.210 Feasibleness of conversion was indicated via thermodynamic analysis involving entropy, Gibbs free energy and enthalpy.

Keywords: Pyrolysis, Kinetics, mechanism, Scenedesmus quadricauda

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List of Abbreviations

S. Q	Scenedesmus quadricauda
EDX	Energy-Dispersive X-ray
EWC	Equilibrium Water Content
FT-IT	Fourier Transforms Infrared Spectroscopy
SI	Salt Index
SRF	Slow-Release Studies
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
PA	Proximate Analysis
UA	Ultimate Analysis
WR	Water Retention
WA	Water Absorbance
XRD	X-ray Diffraction
BC	Biochar

Chapter 1 – Introduction

1.1 Biofuel

Fuel derived from animal waste, algae, or plant material is known as biofuel. Unlike other such as fossil fuels, biofuel is a way toward renewable energy. With the increase in global population, to meet up energy requirement alternative source of energy required to improve quality of life. for this purpose, Biofuels have the potential to meet the global energy requirements. At present, Fossil fuels are the main energy source; on the other hand, use of fossil fuel is creating environmental issues and they are unsustainable. Hence, to address this issue it is ultimately required to substituted fossil fuels with renewable energy sources such as biofuels are a potential source of green energy [1]. In Figure 1.1 different ways to obtain biofuels from biomass are shown.

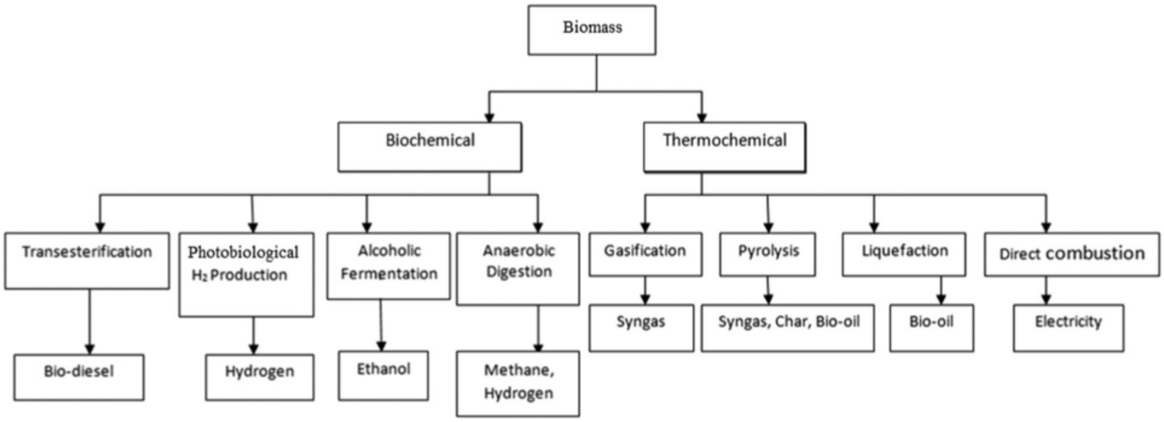


Figure 1.1 Biomass conversions methods

Through different processes as chemical, thermal, and biochemical conversion, Biofuel obtains from biomass. Conventionally, biofuels obtain from food material such as sugar, starch, or vegetable oil. later on, non-food feedstock material like lignocellulosic or agricultural residues used for the production of biofuels requires more land for cultivation. the algae belong to third-generation biofuel feedstock. Through different processes as chemical, thermal, and biochemical conversion, Biofuel obtains from biomass. Conventionally, biofuels obtain from food material such as sugar, starch, or vegetable oil. later on, non-food feedstock material like lignocellulosic or agricultural residues used for the production of biofuels requires more land for cultivation. the algae belong to third-generation biofuel feedstock. They grow faster, less nutrients require, no arable land requires, they can grow in fresh water and sea as wall, helpful in capturing carbon dioxide and clean freshwater , they easily converted into biofuel and provide a good yield as compared to conventional biofuel sources [2].

During COVID 19 pandemic, nuclear energy and fossil consumption fell, but due to low cost operating, the demand for renewable energy increased, recently, in 2020, the erection of new plants and expansions capacities have been observed [3].

WOS (Web of Science) search for a topic say “Algal " or " Algae " was carried out on 19 December 2020, during collection of all of the citations and chemical index which observed 116,868 records. The Web of science different categories for the obtained records was displayed and the overlay is shown in Figure 1.2

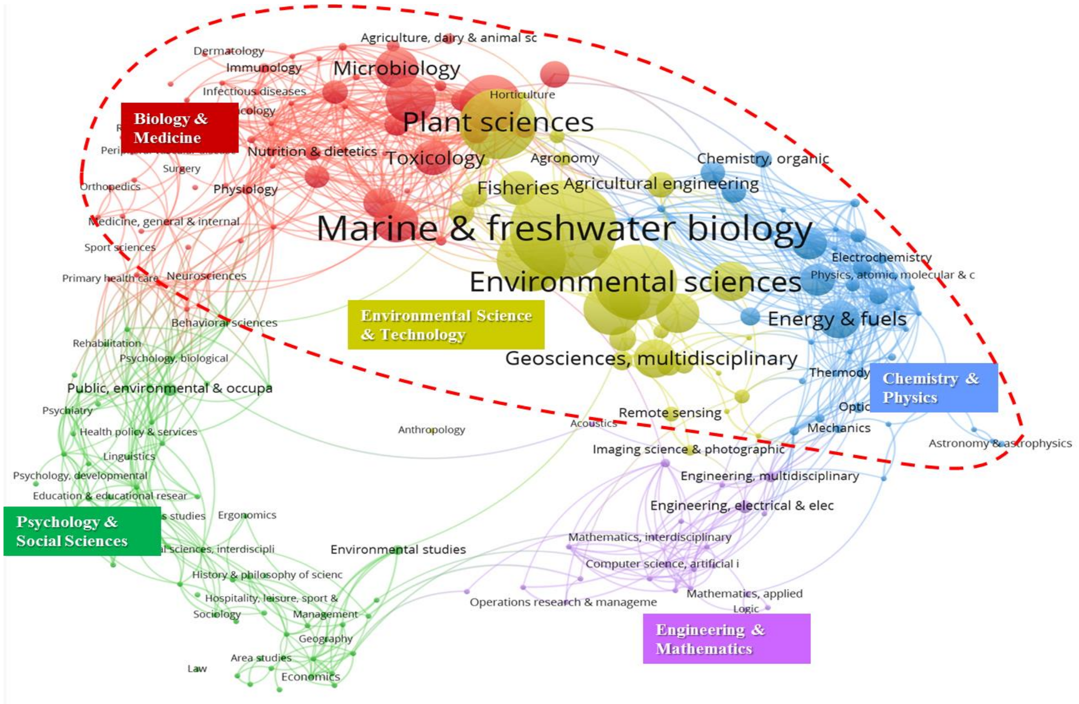
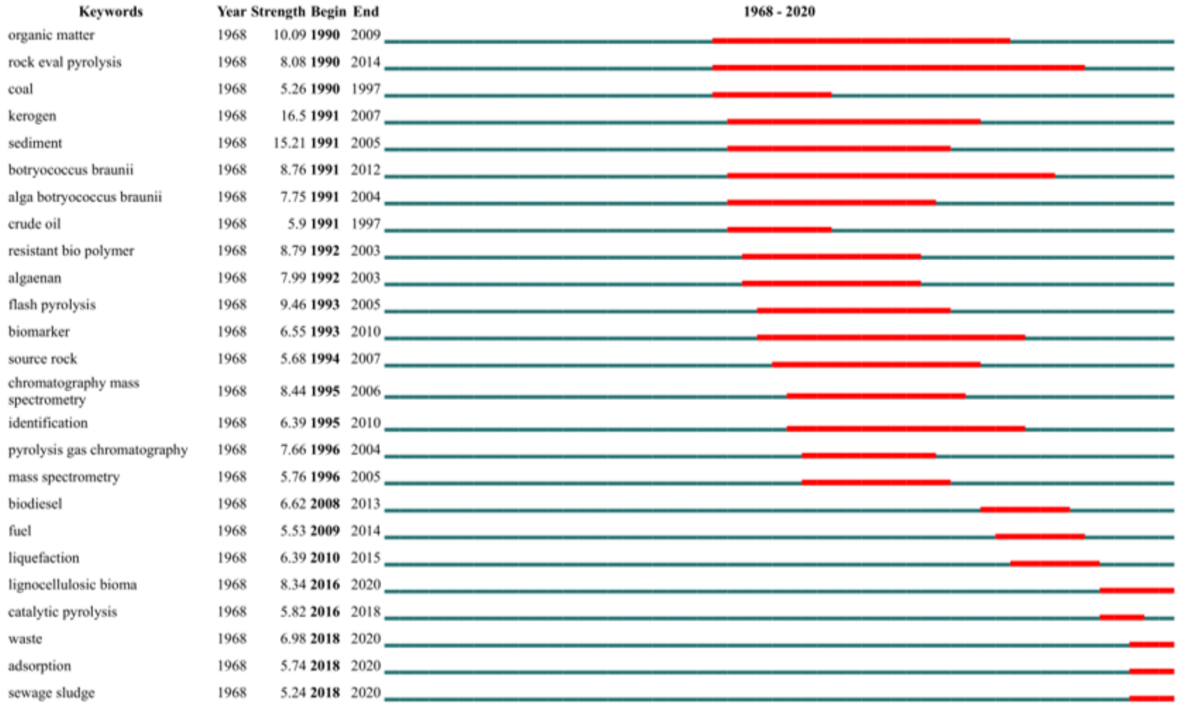


Figure 1.2 Different Categories of WOS

It can be observed that most of the burst started near 1990, and showing the start of 3rd generation of biofuels. 10.150 is strongest burst if citations for “sediments” whereas “rock eval pyrolysis” gained the longest citation burst in the span of 1990-2014. One of the present citation bursts including keywords “catalytic pyrolysis”, “waste”, “adsorption”, and “sewage sludge”. Major citation burst of keywords arose around as it can be seen in Figure 1.3. and it also indicates starting of 3rd generation biofuels.



Keywords	Year	Strength	Begin	End
organic matter	1968	10.09	**1990**	2009
rock eval pyrolysis	1968	8.08	**1990**	2014
coal	1968	5.26	**1990**	1997
kerogen	1968	16.5	**1991**	2007
sediment	1968	15.21	**1991**	2005
botryococcus braunii	1968	8.76	**1991**	2012
alga botryococcus braunii	1968	7.75	**1991**	2004
crude oil	1968	5.9	**1991**	1997
resistant bio polymer	1968	8.79	**1992**	2003
algaenan	1968	7.99	**1992**	2003
flash pyrolysis	1968	9.46	**1993**	2005
biomarker	1968	6.55	**1993**	2010
source rock	1968	5.68	**1994**	2007
chromatography mass spectrometry	1968	8.44	**1995**	2006
identification	1968	6.39	**1995**	2010
pyrolysis gas chromatography	1968	7.66	**1996**	2004
mass spectrometry	1968	5.76	**1996**	2005
biodiesel	1968	6.62	**2008**	2013
fuel	1968	5.53	**2009**	2014
liquefaction	1968	6.39	**2010**	2015
lignocellulosic bioma	1968	8.34	**2016**	2020
catalytic pyrolysis	1968	5.82	**2016**	2018
waste	1968	6.98	**2018**	2020
adsorption	1968	5.74	**2018**	2020
sewage sludge	1968	5.24	**2018**	2020

Figure 1.3 Strongest citation bursts of keywords

Different type of feedstocks of biomass give different biofuels yields as it can be seen in **Error! Reference source not found.**.

Table 1.1.1 Biomass feed stocks and biofuel produced

Feed stocks	Country	Biofuel	Reference
Soyabean, palm oil, sugarcane	Brazil	Bio diesel, ethanol	[4]
Sunflower, rapeseed, wheat sugar beat, barely, landfill, sewage, waste of food	EUA	Bio gas, Ethanol and biodiesel	[4]
Sorghum, corn, soyabean oil	EUA	Biodiesel and ethanol	[4]
Palm oil, cotton oil, molasses, wheat and sugar can	Australia	Biodiesel and ethanol	[4]
Wheat and corn	Canada	Ethanol	[4]
Wastewater and vinasse	Australia	Biohydrogen	[5]
Wastewater and cheese whey	Australia	Biohydrogen	[1]
Corn, rice, potato, cassava sweet and jatropha	China	Ethanol and biodiesel	[4]

1.2 Algae

Algae is a simple, aquatic, non-flowering plant as it is shown in Figure 1.4. It possesses chlorophyll but lacks true roots, stems, vascular tissue, and leaves. Algae can be found in an environment that ranges from rivers, oceans, ponds and lakes and also in snow. It is usually green because of chlorophyll, but it is present in many different colors. For instance, algae that are found in snow contain additional carotenoid pigments l, hence they show distinctive red hue color surrounding snow

Figure 1.4 Diverse group of photosynthetic organisms

1.3 Types of microalgae

Algae has many types. Few of the Algae type are:

1.3.1 Red Algae

It is known as Rhodophyta; it is found in freshwater as well as marine ecosystems. The red color of the algae is due to pigments phycoerythrin and phycocyanin. While Other pigments such as “chlorophyll a” provide green. But they lack beta-carotene or chlorophyll b.

1.3.2 Green Algae

Photosynthetic pigments chlorophyll b and a, auxiliary pigments are found primarily in green algae such as beta carotene and xanthophyll also present which give it a green appearance. They are large and exist in an informal grouping. other species form a symbiotic relationship with algae and use algae photosynthetic products in its group, Members are multicellular, unicellular, flagellates, and colonial. Well-known green algae include Ulothrix Spirogyra and Ulothrix.

1.3.3 Blue-green Algae (Not an algae)

These types of algae are a well-known type of algae. However, it is not included in the algae group because it is prokaryotes and algae contain eukaryotic organisms. It is also called as cyanobacteria; they live in aquatic or moist environments similar to other algae. Its environment includes dams, reservoirs, rivers, lakes, creeks, and oceans. Photosynthesis process provide them required energy. Ecologically, these algae perform significantly in the provided environment by fixing the N in the mud. Hence, they are known as N-fixing bacteria. E.g., Anabaena, Nostoc etc.

However, some other types of blue-green algae have acidic effects on living things. Either they can be hepatotoxic (causes liver failure) or neurotoxic (affects the nervous and respiratory system, and cause paralysis). Moreover, some can act as indicators by signaling pollution and environmental health.

Classification of microalgae

Different types of microalgae are found and can be classified on different basis we have selected algae that are classified on the basis of color i.e., Green, Red, Brown and blue green algae and habitat i.e., fresh, marine. Some microalgae are listed in table 1 based on their usage as biomass for production of energy.

Due to having an aquatic habitat (including freshwater and saltwater) the requirement of land for its growth is not a concern. Adding to that, for the sustainability of aquatic ecosystem and balance of nutrients in that ecology it is vital that algae should be grown on this habitat and then removed. The removed microalgae have been used as biomass in different conversion process for the production of biofuel and syngas. In **Error! Reference source not found.** various microalgae type their color and habitants are shown.

Table 1.2 Various micro-algae characterized on the basis of its color and habitat list [6-28]

S.NO	**ALGAE TYPE**	**COLOUR**	**HABITAT**
1	Nannochloropsis oceanica	Green	Fresh Water
2	Auxenochlorella pyrenoidosa	Green	Fresh Water
3	Arthrospira platensis	Blue-Green	Alkali
4	Schizochytrium limacinum	Light Brown	Marine
5	Ulva prolifera	Green	Marine
6	Saccharina japonica (Areschoug)	Brown	Marine
7	Lemna minor (duck-weed)	Green	Fresh Water
8	Pyropia yezoensis	Red Algae	Shallow Water
9	Chlorella vulgaris	Green	Fresh Water
10	Dunaliella tertiolecta	Green	Marine
11	Nannochloropsis oculata	Green	Marine
12	F. serratus	Brown	Marine
13	S. almeriensis	Green	Fresh Water
14	Spirulina algae (ALG)	Green	Fresh Water
15	Enteromorpha intestinalis	Green	Marine
16	Derbersia tenuissima	Green	Marine/Salt Water
17	Oedogonium (N+)	Green	Fresh Water (N2 Enriched)

18	Oedogonium (N-)	Green	Fresh Water (N2 Deficient)
19	Scenedesmus sp.	Green	Fresh Water
20	Chlorella pyrenoidosa	Green	Fresh Water
21	Botryococcus	Green	Fresh Water

1.3.4 Microalgae characteristics

Characteristics of microalgae in general resemble with animals as well as plants.

For example, algae photosynthesize just like plants and they have special type of cell organelles, and structures just as centrioles and flagella and it is only present in animals. Following are some of general algae characteristics.

1. Microalgae can perform an activity of photosynthesis.
2. It either can be multicellular or unicellular microorganisms
3. Algae does not have a properly defined body, and its structures are like leaves, stems, or roots are not present
4. They are mostly present in an environment of adequate moisture.
5. Algae can reproduce in both sexual and asexual formats. Spore formation takes play in Asexual reproduction.
6. These are mainly living freely, sometimes they have a symbiotic relationship.

1.3.5 Cultivation of microalgae

Apart from natural growth, microalgae can also be cultured. The usage of microalgae as biofuel is considered due to various positive prospects such as

1. Microalgae plays a role of O sustainable producing system
2. Microalgae, do not clash with food chain of human and animal
3. They are rich in different compounds such as carbohydrates, proteins, lipids and pigments.

4. Culturing can be done using fresh water, sea water, saline water, brackish and waste water.
5. The absence of complex reproductive organs and simple cell division helps in their fast growth
6. As far as sunlight is available, microalgae will sustain their capability to grow throughout the year [29-36].

The culturing of microalgae in an open system is most providential technology. Open systems neither require any specialized technology nor it require specified land. Due to open systems not only, the uncultivated land can be used for microalgae cultivation but the productivity rates in the worst case are still three times more than other biomasses cultivated on that land [13]. For obtaining specific biomass productivity (g/m2 *d) different design models are being adopted. However, the successful cultivation of microalgae on large scale requires some parameters to be considered [13]

- Availability, cost and suitability of the land
- Microalgae types (strain, size of the cell, carbohydrate and lipid content, harvesting, and the processing)
- Algal product value
- In order to generate biomass high volume cost of the raw material
- For cultivation amount of water required.
- Climate conditions
- LCA (Life cycle assessment) studies.

Recently, different studies have been carried out in which nanotechnology is being used for preparing and enhancing techniques for micro-algal cultivation harvesting and extraction of biofuels. Nano-additives are also added to microalgae to intensify enzyme immobilization due to which the surface area is increased and in return the yield of biofuel is be increased. Different nanoparticles like multi walled carbon nanotubes (MWNTs), graphene oxide and oxidized multi-walled carbon nanotubes (O-MWNTs) etc. are being used in which O-MWNTs showed highest yield [33, 35]. This paper is focused on the production of syn-gas from the cultivated microalgae which can be utilized for the production of energy by converting it into gaseous fuel.

1.4 Thermochemical conversion of microalgal biomass

The process in which organic contents of biomass are decomposed into biofuels at higher temperature is known as Thermochemical conversion. It is very simple process than processes which are used for bio oil production like biochemical and chemical process. [37]chemical process requires an additional step of purification into order refine biomass prior to chemical conversion and biochemical process depend on biocatalysts in order to achieve conversion like microbe cells and enzymes. And sometimes many days are required to get required biochemical conversion [37]. Thermochemical processes need only heat or physical catalysts so they give more profit and this can be applied almost every feedstock available. They do not require any chemical addition and very little time is required to carry out reaction.in this method product and energy formed are affected by chemical reaction and temperature[37].

Mostly used processes of thermochemical are direct combustion, pyrolysis, gasification and liquefaction.[38].

1.5 Technological challenges

We can utilize microalgae in place of fossil fuel due to their greater productivity of oil content than other biomasses and they can be processed more easily than lignin[39]. Microalgae pyrolysis is very affective technique to get oil, but it has also some problems associated with algal feedstock. If we check it economically oil producing through algae is not viable because we need high cost to obtain oil production. If we wish to use it in commercial manners then we need to reduce its production cost.[39]

In order to reduce cost which is used to culture the microalgae, we should algal biomass which has better photosynthetic qualities or by utilizing wastewater to get nutrients. Also the species which are modified could be utilized for better cost control in order to use microalgae as feedstock for biofuel.[39, 40]

Also harvesting of algae very costly step to produce microalgae, because microalgae are very little cells and are dispersed in cultural medium. There is a need of large room space for centrifuge to separate these species in order to start or end, his makes this process more costly because high power is required. From different studies it is concluded that step of dewatering consumes up to 69% of power for given instant of time[41].

The algal feedstock which is used in the pyrolysis also needs greater amount of water for cultivation and this is biggest challenge associated with it. And the feedstock which is to be used in pyrolysis should have moisture content in the range of 15 to 20% or lower than that[42].

Lowering of moisture content requires more energy .drying of algal mass is very tough step while getting biofuel from it[42, 43].

The total amount of energy which we get is lower than energy that is used fir dewatering (‘NER < 1.O’)[41]. Acidic type of oil is obtained from microalgae which is very unstable.it is viscous and also has some of solid contents in it and chemically dissolved water in it. Oil which is gained from microalgae is acidic in nature and is unstable. Its viscosity and also it has solids. And also, water is chemically dissolved in it. Therefore, that it is required to maximize the production of the bio oil through algal pyrolysis[44] .

The presence of sustainable algae resources is very important challenge which is attached with algae. Biomass is a natural source of renewable energy. Even though for getting energy bio-fuel is a renewable resource, it’s not reliable source for energy. In recent bio refinery, biomass and the fuels that are being utilized together.[45].

Chapter 2 -Literature Review

- Vikal Vasudev et.al (2020) carried out pyrolysis of algal biomass and determined kinetic triplets and also did thermodynamic analysis. In this work master plot was utilized to find the kinetic model. Researcher found that pyrolysis reaction was transition b/w diffusion, nucleation and kinetic models that are order based. pyrolysis process was described by a proposed kinetic model equation and showed a single differential peak of TGA. [46]
- Sumona Das et.al (2020) algae from power plants and did assessment of growth kinetics and **bio**-char production from slow pyrolysis process. In this study growth kinetics was described by a Haldane model. When temperature is lowered from 700 to 300C biochar yield increases from 29 to 44%.[47]
- Xiaoke Ku et. al. (2019) studied kinetic and pyrolysis characteristics of algal and lignocellulosic biomasses. The finding of the studies is that Z(α) master plots suggested the nucleation model dominated at lower and higher conversion stages and the diffusion played a key role in the intermediate stage of lignocellulosic biomass. Ho
- Quang et .al (2017 did comprehensive study on pyrolysis kinetics of microalgal biomass in this study single, two and three models of reaction do not fit the shoulder and peaks properly so they are not good for the pyrolysis of algae. Experimental data and model have better combination when we the number of reaction are higher. [49]
- N.I Chernova et. Al (2020) studied manufacturing of gaseous products by pyrolysis of microalgal biomass. The findings of this study were that proportion of high calorific components of the gas mixture (H2, CH4 and Co) increase with the temperature increase. [50]

In **Error! Reference source not found.** literature review for TGA coupling of microalgae is given where habitant for microalgae and operational parameters for TGA coupling are given.

2.1 1TGA coupling for microalgae and operational information

Microalgae	**TGA coupling**	**Operational information**				**Reference**
Freshwater/ Wastewater	TG-FTIR/TG-MS	Initial mass (mg)	Max decomposition temperature (°C)	Heating rate(°C/min)	Gas flow (mL/min)	
Freshwater	TG-MS	10	1200	5,10,20,30	-	[51]
Freshwater	TG-MS	2-3	800	10,15,20,30	500	[52]
Freshwater	TG-MS	2-3	800	10,15,20,30	500	[52]
Freshwater	TG-FTIR	5	800	10	100	[53]
Freshwater	TG-GC-MS	20	900	20	70	[54]
Freshwater	TG-FTIR	10 ±0.3	800	10,20,40	80	[55]
Freshwater	TGFTIR/GC-MS	5 ± 0.1	900	20,30,40,50	80	[56]

2.1 Pyrolysis

It is one of the oldest technology or say technique to produce biofuels from variety of biomass. In pyrolysis biomass is subjected to high temperature and pressure under Inert conditions likely zero content of oxygen present to produce bio fuels. Mostly liquid fuels are produced by pyrolysis but in this case bio char. A solid fuel is being produced from microalgae. Temperature ranges between 350 to 650C for pyrolysis process. There are different types for pyrolysis which base on resident time, temperature, heating rate and size of particles. Different pyrolysis process are slow pyrolysis, fast and Flash[57]. Bio Char production through pyrolysis and gasification of biomass under presence and absence of oxygen is shown in Figure 2.1

If large quantity of Bio Char production is needed then slow pyrolysis is more suitable. Because in this process temperature increases gradually and Biomass degrade slowly and this provides longer residence time to biomass so bio char is formed then bio oil and gas [58]. Pyrolysis has complex reaction mechanism so it is converted into three steps. First step is dehydration of biomass, then primary char is produced with some residues of biomass also some volatiles and gases are lost too and last step is formation of 2ndary bio char by slow decomposition of primary char which is rich in carbon content [59]

Properties of char are also influenced by pyrolysis temperature like functional groups of surface and surface area. Bio char has greater surface area and much more porosity at elevated temperature because of breakdown of aliphatic alkyls and Ester groups of a compound which is organic in nature[60].

Bio char formed is thermally stable and hydrophilic too. And Bio char which is produced at low temperature is hydrophilic in nature. If bio char is produced at high temperature chemical bonds get rearranged and on surface new functional groups are formed like pyridine phenol carboxyl, and lactone. Functional group which are newly formed can act as acceptor of electron. In low pyrolysis temperature structure of graphene is simulated by biochar produced and lesser functional groups are being exposed[61, 62].

When higher quality of Bio fuel is needed then fast pyrolysis is performed. When Scenedesmus sp.alga goes fast pyrolysis at 500c and residence time of vapors is 2.0s then 55% bio oil is produce and from Chlorella vulgaris under fast pyrolysis at temperature of 500c 53.0% bio oil is produced[63]. In Figure 2.1 conversion cycle for biomass is well explained.

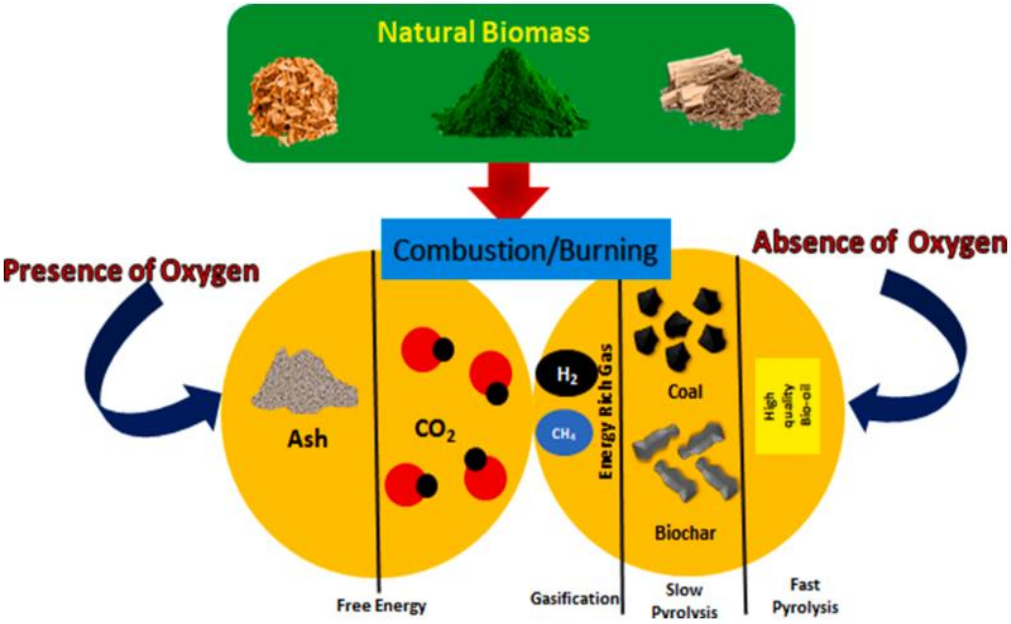


Figure 2.1 conversion cycle of natural biomass into biofuel

Different pyrolysis parameters and factor affect pyrolysis process as shown in **Error! Reference source not found.**

2.2 Pyrolysis Parameters and Factors Affecting

Sr. No	Process	Temperature/◦C	Residence Time	Heating Rate/◦C/min	O_2 Presence	Ref.
1	Slow	<600	300-550s	1-10	No	[64]

2	Slow	300-650	5min-12hrs	10-30	No	[65]
3	Slow	400-500	5-30mins	0.1-1◦C/s	No	[66]
4	Slow	300-400	6 hrs	-	No	[67]
5	Slow	800		5-20	No	[68]

2.2 Factor affecting algal biomass pyrolysis

Algal biomass pyrolysis is influenced by a number of factors

Many factors like feed stock and temperature and composition 9(‘moisture content, chemical [69]composition, and also size of particles), flow rate of gas heating rate ,resident time and catalyst can affect pyrolysis product’s composition and biofuel yield[69]. order to better quality and best yield of products there are some of parameters that should be in optimum condition for every feed stock that is used in pyrolysis.

Higher heating rates, for example, can speed up decomposition and boost bio-oil production. When using traditional pyrolysis techniques, it is essential to achieve high heating rates. At high temperatures, the vapor phase's longer residence time will result in secondary decomposition.

The vapor must therefore be removed and quickly reduced to bio-oil from the reactor at the appropriate flow rate of carrier gas.

In general, high heating rates, moderate temperatures and low residence times are the preferred conditions for bio-oil production. This section discusses the influence on pyrolysis of algae of the composition of feedstock, particle size, reactor temperature, heat intensity, duration of residence and flow of gas.

2.2.1 The impact of composition of feedstock

In the pyrolysis process yield and composition of products is altered by, the chemical composition and structure of the feedstock. Algal biomasses have a wide range of protein, lipid, and carbohydrate material, resulting in a wide range of product compositions. Lipids are a form of fat. Algal biomass provides efficient production of Bio diesel. , whereas algal source which is high in carbohydrate content can be utilized as a source of carbon in producing bioethanol or bio methane[70]. Hong et alresearch. On the biological yields of oil and the compositions extracted through pyrolyzes, one chlorella and two spirulina have been shown to provide in comparison with carbohydrate-rich porphyrene, macroalgae that contain up to zero bio-oil (almost 2.50%wt. percent) but greater oil yields in comparison to carbohydrate-rich porphyrene (85. 0 wt. percent), bio oil from another source or analysis was compared with quick pyrolysis of three micro algae and duckweed of four aquatic plant types [71]The findings showed that due to their identical structure and characteristics , pyrolysis of these three microalgae provided similar results. But duckweed pyrolysis provided low bio-oil (pyrolytic) and greater carbohydrates. In addition, duckweed which has a high oxygen content and lower energy had lower quality of yields Studies have shown that algal biomass is very different in pyrolysis than Lignocellulosic biomass. Algal Biomass carbohydrates, proteins and lipids could be pyrolyzed with a very high lignin content than Lignocellulose's main components, resulting in a higher bio oil yield[72].

2.2.2 Rate and temperature effect of heating

In pyrolysis of biomass heating rate has great impact because it effects the final composition and the structure of product. With low heating rate there are minimum chances of 2ndary pyrolysis and Biomass thermal cracking is abstained which provides greater formation of Bio Char.

Faster heating rate enhances the potential bio to degenerate into a gaseous substance and prevents repolymerization The vapor of lipid algae also increases the bio oil formation at low temperatures[73]. The temperature of pyrolysis also has a significant influence on outputs and product composition. Through the formation of more volatile materials at elevated temperatures, high temperatures minimize pyrolysis char yield. As discussed above, the biomass yields of algal biomass reach a maximum of 400c and 550c at temperatures. Cracking reactions where hydrocarbons of greater Molecular weight are converted into the very small ones leading to decreased bio-oils are significantly promoted by temperatures over 550 °C Increased temperatures further increase the content of carbon outputs and PAH production. Bio-oil production in micro algae Desmodesmus sp [74] investigated bio-oil production. At various temperatures. Compared with bio-oil formation through algae pyrolysis Desmodesmus sp. The highest bio-oil content could be generated by pyrolyzing the sample at 750°C (32.07%) at 650°C. The higher temperature could however more easily contribute into the production of pollutants (N and PAHss). The study at Zhong Et al. [75]shows that maximum yield of algal bio-oil (59%), at different temperature ranges that is from 300 to 700 occurred at 500c. It was defined that high temperature of pyrolysis enhanced quality of bio-oil when its heating rate and content of hydrocarbon was enhanced. But products which are unwanted their quantity increased which include N compounds and PAHs.

2.2.3 Particle size effect

Particle size is very effective parameter in pyrolysis process due to its role as controller of heat transfer rate to bio mas. Characteristics and yield of Bio oil is affected by Size of particle and also it overcomes issues related heat transfer. When size of particle is bigger it Increases thermal gradient and lowers yield of Bio oil because 2ndary reaction occurs and high bio char content is produced. [76]blue algae blooms give maximum liquid fuel yield without even cost of grinding. [76] when size of BGBA is decreased up to greater extent like from 54.98 % to 42.89 % amount of gas producing decreases from 20.49 % to 18.99 %. And yield of Bio Char reduces in greater amount from 24 % to 18 % which is related with heating rate provided to particles. As size of BGBA enhances the distance of resistant between the surface of algae particles and center of particle increases. And slows down the faster transfer of heat from hot to cold bio mass, which makes reaction of pyrolysis incomplete. Campanella and Harold [71]determined same outcomes from Larger particle size on bio oil formation. Although from some studies it is concluded that size of algal particle dose effect has no impact on products of pyrolysis. [41, 77]. Ertas and Alma[77] have studied the impact on the outputs of pyrolysis products of 0.25–1.60 mm of laurels (Laurus nobilis L.) and have shown that the outputs of bio oil and char are essentially unrelated to those of particles. These incompatible findings clearly demonstrate the need for a more comprehensive analysis of the pyrolysis process impact of the algae particle size. Vapor resident time has impact on connection between primary vapors and the char. And 2ndary reactions strength and volatile products qualities are determined by this.[78]. If resistance time is high bio char production will be higher. Greater residence time of vapors provides enough time to components of biomass for the reaction and repolymerization, on the other hand smaller resistance time makes repolymerization incomplete, which will produce small amount of bio char[69]The time for vapor resident is mainly effected by gas flow and heating rate and the temperature. So the resident time and solid product yield enhances. [79]Wang et al.[76] displayed a dominant on composition of Bio oil which results from seaweed pyrolysis on the vapor residence time. The aromatic hydrocarbon chain breaking will enhance the time frame of longer residency. In result volatiles 2ndary reaction is more casual during long vapor resident time the amount of hydrocarbon, ketones and alcohols enhances.

2.2.4 Gas flow rate effect

Another major parameter affecting the distribution of pyrolyze products is the carriers of gas flow rate. In the phase of pyrolysis, the air does not provide only inert carrier gas but can also remove vapors as the reactor passes through. This decreases the time of the vapor residence and reduces the volume of cars. If the vapors formed are not purged out during the pyrolysis of biomass, then the secondary reactions that lead to changes in the pyrolysis products nature and composition will occur[80].The gas which is being used as carrier should be inert in nature and not engage in any kind of reaction. N (Nitrogen) is the more widely gas being utilized as a carrier gas in processes like pyrolysis, due to advantages such as low cost and easy availability[69]. Several studies have been published that look into the impact of carrier gas flowing rate on the product distribution of pyrolysis.

2.3 Advantages of producing bio-oil via microalgae pyrolysis

Although one of the best processes to produce bio-fuel through algae are thermochemical processes but they have flaws too. Like their efficiency of gasification is very small and gasses are their main product. As there is very high content of water present in biomass feed there are maximum chances of lowering gaseous productivity. Process producing liquid fuels is very complex and for Liquefaction special type of equipment are required which are costly. Production of energy via direct combustion is very small and heat produced could not be saved so we have to make use of it immediately. Pyrolysis is a better technique to produce oil fuels which are gaining importance day by day. Advantages of this technique are following as compared to other techniques. Bio oil is the main product of pyrolysis and sometimes 75% bio–oil can be obtained.

If bio-oil is produced via fast pyrolysis it has greater HHV in comparison to most of fossil fuels, it can be up to 42 MJ/KJ.

Bio oil has 81.56% carbon content and 8.8% hydrogen while oils which we get from fossil fuels have carbon value of 8 to 88% and H 10 to 14% [81] . In fast pyrolysis resident time is very small so it reduces cost of operation and very high bio oil content is produced. [82] By making some adjustments in parameters of operation we can obtain that product which is desired like liquid, gas or bio char. In bio oil amount of N and S is small and storage of oil is also easy[83]. Even if biomass is not processed we can get better products through process of pyrolysis say 80.00%. [84] Different microalgae have different kinetic mechanism and also pre-exponential factors as shown in **Error! Reference source not found.**

2.3 kinetic mechanism and pre-exponential factor for different microalgae specie

Microalgae	Kinetic mechanism	Ea (1st stage/2nd Stage) KJ/mol	A (pre-exponential factor)	References
Scednedesmus quadricuda	single step	77.95 (±3.12) low 73.26 (±17.93) high	4.86E4 (±2.24E4) low s-1	[85]
Spirulina maxima	single step	132.62 F.F. I	1.32E3 (±2.61E3) high s-1	[86]
Chlorella vulgaris	-	143.77 M.D. A	8.7 · 109 –4.1 · 1023 s −1	[87]
Isochrysis galbana	-	136.89 M.I. P	1.2 · 1012–6.9 · 1022 s −1	[87]
Nannochloropsis gaditana	-	135.6-337.1 148.4-309.4	1.1 · 1011–7.2 · 1026 s −1	[87]
Nannochloropsis limnetica	-	137.4-373.0 123.2-295.6	1.1 · 109 – 1.5 · 1021 s −1	[87]

Phaeodactylum tricornutum	-	145.0–452.2	5.3 · 1012–7.9 · 1031 s −1	[87]
Spirulina platensis	-	145.0–452.2	7.8 · 106 – 5.8 · 1015 s −1	[87]

Chapter 3 - Research Methodology and Materials

3.1 Methodology

In the project, Bioenergy potential of quadricauda is determined through pyrolysis by using thermodynamic and kinetic analyses. In this work microalgae (S. quadricauda) were cultivated in photobioreactor. Actually, algae were obtained from Algaetech, Malaysia. Inoculation of algae was performed at 20 ml and it was cultured for 10 day and recovered by centrifuge. Then Scenedesmus quadricauda was subjected to thermogravimetric analyzer.

3.2 Equipment used in research

There is some equipment that are used in any of research

- Photobioreactor
- Beakers
- Conical flask
- Centrifuge
- Digital weight balance
- Conductivity meter
- Nitrogen cylinders

3.2.1 Photobioreactor

A reactor which uses sun light for the Cultivation of phototrophic microorganisms is known as photo bio reactor as shown in Figure 3.1. In order to generate biomass through light and carbon dioxide microorganisms utilize photosynthesis. In this reactor an artificial environment is created and specified conditions are controlled carefully for different species. So, in photo bioreactor growth rates are very high and purity level is also higher than other same habitual. In hypothesis biomass that is phototrophic can be obtained from waste water that is rich in nutrients.

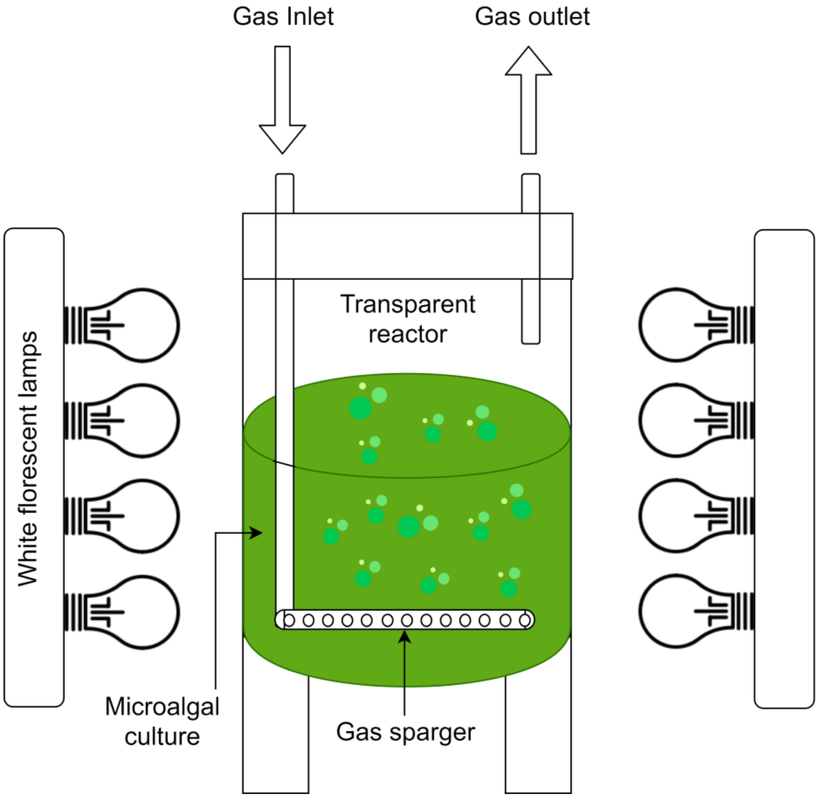


Figure 3.1 Photobioreactor

3.2.2 Beakers:

A simple container used for stirring, mixing and liquids is known as beaker as shown in Figure 3.2It is generally utilized in many laboratories and it was at first made in 1453. Shape of beakers is cylindrical and with a flat bottom and a small spout for aid in pouring. Beakers are available in a wide range of sizes, from one milliliter up to several liters

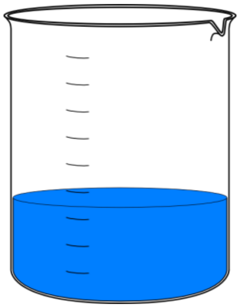


Figure 3.2 Beaker

3.2.3 Centrifuge

A machine which uses centrifugal force for separation of constituents of a sample on the basis of their density is known as centrifuge as shown in Figure 3.3. A strong centrifugal force is produced when centrifuge starts spinning. Separation can be obtained through earth gravity but centrifuge is used to get rapid laboratory results.

Figure 3.3 Centrifuge

3.2.4 Digital weight balance

In simple words it is a device which is used to calculate the weight of a material shown in Figure 3.4. Since it’s a digital device the measurement is very accurate. However before using the device, it should be calibrated at 0.00 gram to ensure ideal weighing. The balance was used during the experimentation for the accurate weighing of biochar throughout the whole methodology.

Figure 3.4 Digital weight balance

3.2.5 Fluorescent bulbs

A lamp as shown in Figure 3.5 with small pressure and mercury vapor gas discharge lamp which utilizes fluorescence in order to obtain visible light is called fluorescent bulb. Mercury vapor get excited by the electric current in result ultraviolet light with short wave is produced which cases the glow of phosphor coating present inside the lamp.

Figure 3.5 Fluorescent bulb

3.2.6 Conical flask

It is cone shaped flask with a cylindrical neck and a round bottom. It was invented by German Chemist whose name was Emi Erlenmeyer. It is used to prepare concentrated solutions and also used for chemical analysis as shown in Figure 3.6.

Common features of conical flask are followings

- Hollow design
- Resistant chemically
- Compact
- Reliable

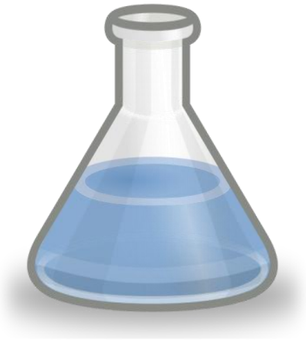


Figure 3.6 Conical flask

3.2.7 Conductivity meter

A conductivity meter is shown in Figure 3.7. It measures electrical conductivity of solutions.it give precise and reliable measurements.

A potentiometric method and four electrodes are employed by a usual conductivity meter that is used in laboratory. Cylindrical electrodes are used often which are arranged concentrically. These electrodes are made from platinum metal. In this equipment current applied to outer pairs of electrodes is alternative. And the electrode pair which is inside of meter their potential is calculated. We can find conductivity from distance between electrodes and the surface area of electrode with the help of ohms law. We employ mostly inductive method to conductivity probes which are used in industry because in these electrical parts are not wetted by the fluid. Two coils which are coupled inductively are utilized. One of them produces magnetic field because it is driving coil and it is supplied to exactly known v. And the 2nd makes 2ndary coil of a transformer. In transformers 2ndary winding one turn is formed by liquid which passes through a channel in the sensor. And output of that sensor Is induced current. We can also utilize a conductivity sensor which has 4 electrodes and which are made from the material which is resistant to corrosion. One of its biggest benefits is that it has compensation of scaling when compared to inductive sensors. And it can measure lower than 100µS/cm conductivity.

Figure 3.7 Conductivity meter

3.2.8 Nitrogen Cylinder:

Nitrogen acts an inert gas during the process of pyrolysis to provide inert conditions during the whole process and ensure that the process of pyrolysis is carried out smoothly. A nitrogen cylinder shown in Figure 3.8

Figure 3.8 Inert gas (Nitrogen) Cylinder

3.3 Raw Materials

Given below are the raw materials that were used during this project or process.

- Scenedesmus quadricauda biomass
- Nitrogen gas (inert gas)

3.4 Microalgae cultivation

Figure 3.9 depicts the set-up of a segment photobioreactor in use. The photobioreactor was encircled by bright light bulbs that provided the light source. The reactor had a working volume of 5 L (30 cm high, 16 cm interior breadth) and used Blue Green (BG-11) medium. Citrus extract, at 0.1M, was used to achieve a pH of 7.11. Algaetech in Malaysia provided the Scenedesmus quadricauda (S. quadricauda) supply. Independently, a load of green growth was vaccinated at 20 ml and refined for 10 days. After 10 days, the way of life was recovered using axis (Hermle Z206A; 41.8 km/s-2, 5 min) and then resuspended in 1 L of new medium. The stock culture was stored at 5 °C in a dull condition as the inoculum for the following experiments. The fundamental culture trailed the preculture. To ready the microorganism's cell for the premise culture, the patent laws was vaccinated with 100 mL of stock cultural values and perfected for 10 days, shown here in **Error! Reference source not found.**.9

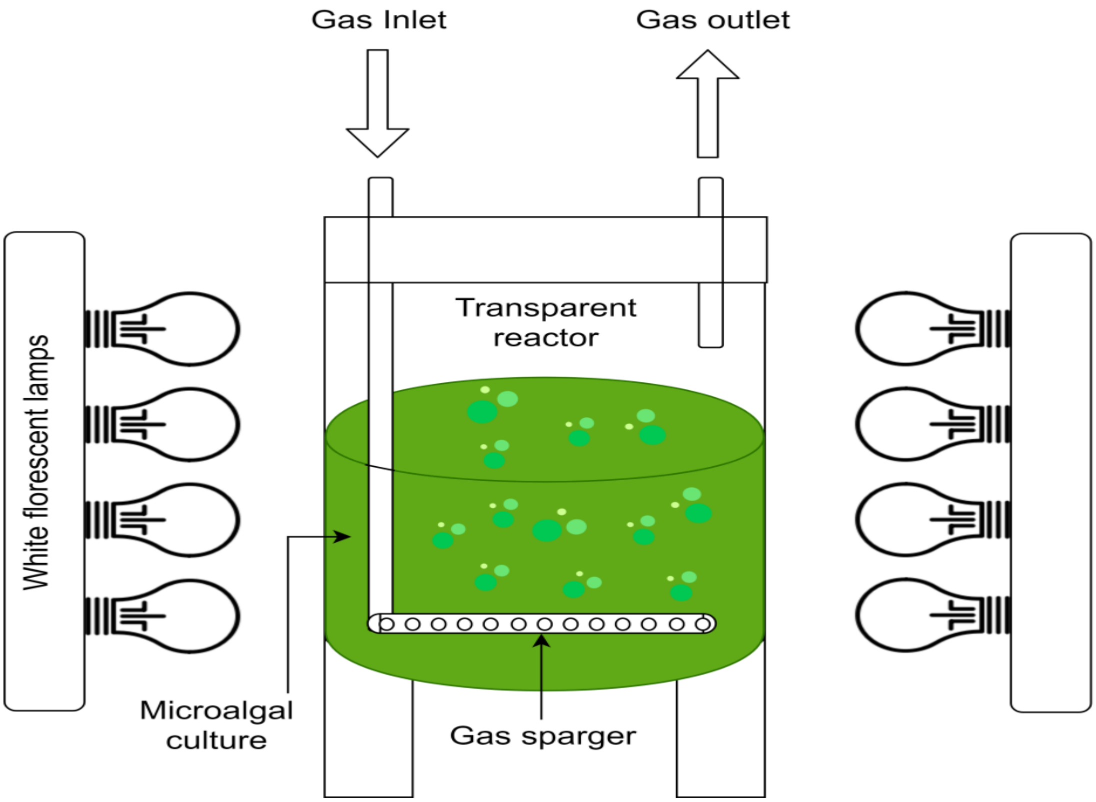


Figure 3.9 cultivation of microalgae

In order to gather (inoculate) the main culture the amount of preculture which was used in this work was 500 ml and 0.22to 0.23 g1/ L of biomass at first (initially) was utilized. And at the temperature of 25C the culture was kept at white light for almost 10 days. Light source which was used for the illumination of culture was giving 10000 lux in average. And temperature was kept at 25C.

3.5 Preparation of sample

A HERMLE centrifuge was used for the centrifugation of solution of 20ml algae for 10 days at the 3500 rpm. And at the temperature of 105C the oven drying of centrifuged sample was carried out for 2 days.

3.6 Thermogravimetric Analysis (TGA):

TG analysis can be used to find thermal the thermal behavior of algae when conditions are inert. In TG and DTG loss of mass of algal samples is checked by increasing temperature and time. With the use of TG and DTG curves temperature at which biomass completely pyrolyzes can be determined. But yield of product distribution is affected by 2ndry reactions. Gaseous products are produced by HTL of algae biomass, these gases include CH4, CO2, CO and H2 also some quantities of C2-C5. Amount of CO2 produced more than other gases as it is always greater for HTL of every biomass. Shift reaction and steam reforming produce CO2. Also, CO2 formation is favored by fatty acids decarboxylation. During steam reforming and water gas shift reaction H2 is also produced but it is very small as compared to CO2, so from this it is assumed that mechanism of production of these gases is different. SJ produces .5 mmol/g of H2. Amount of CO formed is always smaller because initially produced CO is always consumed during shift reaction. CH4 is produced during mechanism reaction at it is small in quantity [13]. In this work TGA was utilized to perform Pyrolysis of S.D biomass. And atmosphere was inert which was kept inert by flowing 200.00 ml/min of nitrogen in continuous matter. Process of TGA was carried out at room temperature to 800C and initial biomass was used in the form of fine dried powder and it was almost 10±3 mg. Different heating rate were applied to samples 10,15,20 and 50C/min and during this loss of mass was recorded with temperature and time. To get minimum restrictions in heat transfer the pyrolysis experiments were carried out at slow heating rates. All of the pyrolysis experiment steps were repeated three times. The data which we obtained from TGA was used to evaluate the thermodynamic and kinetic behaviors at the specific conditions which we used.

Energy of activation in average of PC1 were 77.950 [±03.120]) kj/mol, and pre_ exponential coefficient 4.860E4 [±2.240E4]/s, and n=1.510 [±0.100] and for PC2 E Is 74.260 {±17.930} kj/mol, pre _exponential coefficient of 1.320E03 [±2.610E03] /s, and with n=1.210 [±0.160].

3.7 Assessments of Kinetics

3.7.1 Model free kinetic analysis

In order to calculate the E (energy of activation) via TGA most known methods are iso conversional methods which we call model free methods. And the base of these models is that reaction model always remains identical for a given conversion no matter what the rate of heating is. In these types of techniques starting is always kept simple.

$$\text{Scenedesmus quadricauda} \rightarrow \text{volatiles} + \text{biochar} \qquad (1)$$

from Arrhenius law we can depict its degradation when it is temperature dependent/

$$\frac{D\alpha}{dt}=kf(\alpha)=A\ \exp\ \left(-\frac{E_\alpha}{RT}\right) f(\alpha) \qquad (2)$$

there T represents temperature, all gas constant is denoted by R, and rate constant is described by k, Reaction model is f (a), A is used as pre-remarkable, E_ is the energy of activation

showing conversion via mass loss in fractions.

$$\alpha=\frac{m_i-m}{m_i-m_f} \qquad (3)$$

During thermolysis a linear heating rate $\left(\beta=\frac{dT}{dt}\right)$ a linear rate of heating for the pyrolysis is taken putting β in equation provides.

$$\beta\frac{d\alpha}{dT}=A\ \exp\ \left(-\frac{E_\alpha}{RT}\right) f(\alpha) \qquad (4)$$

for solving differential equation, we should separate different variables

$$\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\ \exp\ \left(-\frac{E_\alpha}{RT}\right) dT \qquad (5)$$

Integration of the equation provides

$$g(\alpha)\int_{0}^{\alpha}\frac{d\alpha}{f(\alpha)}=\int_{T_0}^{T}\frac{A}{\beta}\ \exp\ \left(-\frac{E_\alpha}{RT}\right)dT \qquad (6)$$

In order to determine rate equations which are in the linear relation form many of researchers give approximate solutions. We can divide these equations into two different groups and this is dependent on equation’s final form either it is integral or say differential.

Friedman is a differential strategy and according to Vyazovkin we can calculate energy of activation via lowering $\Phi(E_a)$ by applying the isoconversional integral technique which is nonlinear. And Ozawa–Flynn–Wall (OFW) is isoconversional integrals method’s linear form

Friedman:

$$\ln\left(\frac{d\alpha}{dt}\right)=\text{const-}\frac{E_a}{RT} \qquad (7)$$

OFW:

$$\ln\beta=\text{const-}1.052\frac{E_a}{RT} \qquad (8)$$

Advanced Vyazovkin:

$$\Phi(E_a)=\min\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J[E_a,\ T_i(t_\alpha)]}{J[E_a,\ T_j(t_\alpha)]} \qquad (9)$$

$$J[E_a,\ T_i(t_\alpha)]=\int_{t_{\alpha-\Delta\alpha}}^{t_\alpha}\exp\left[-\frac{E_\alpha}{RT(t)}\right]dt \qquad (10)$$

Variant heating rates are donated by subscript i and j, in conversion $\Delta\alpha$ represents step change. Time required to achieve α-$\Delta\alpha$ and α conversions is. $t_{\alpha-\Delta\alpha}$ and t_α. The absolute temperature for β_i rate of heating at ta is $T_i(t_\alpha)$. And progress of reaction is represented by J which is an integral function.

3.7.2 Model fitting kinetic analysis

If the reaction has single step mechanism and by incorporating a model constraint $f(\alpha)=c(1-\alpha)^n\alpha^m$ and modifying the rate equation, we get

$$\ln\left(\frac{d\alpha}{dt}\right)-\ln[(1-\alpha)^n\alpha^m]=\ln(ck_0)-\frac{E_a}{RT} \tag{11}$$

Standardization is used to obtain the categories n, m, and c.

Parallel independent reactions

For these types of reactions equation of Šesták and Berggren was used.

$$f(\alpha)=(1-\alpha)^n\cdot\alpha^m\cdot[-\ln(1-\alpha)]^p \tag{12}$$

It is possible to adjust the rate equation for 2 components.

$$\frac{d\alpha}{dt}=x_1\cdot A_1\cdot\exp\left(-\frac{E_{a1}}{RT}\right)\cdot(1-\alpha)^{n_1}\cdot\alpha^{m_1}\cdot[-\ln(1-\alpha)]^{p_1}+ \\ (1-x_1)\cdot A_2\cdot\exp\left(-\frac{E_{a2}}{RT}\right)\cdot(1-\alpha)^{n_2}\cdot\alpha^{m_2}\cdot[-\ln(1-\alpha)]^{p_2} \tag{13}$$

Restricting the Sum of the Measured Mistake (SSE) between both the test and expected qualities controls the response ingredients.

$$SSE=\sum\left(\left.\frac{d\alpha}{dt}\right|_{exp}-\left.\frac{d\alpha}{dt}\right|_{pred}\right)^2 \tag{14}$$

The essence of the obtained results can also be verified using Fit (percent), which is described as

$$\text{Fit }(\%)=\left[-\frac{\sqrt{SSE}}{\left(\left.\frac{d\alpha}{dt}\right|_{exp}\right)_{max}}\right]\times 100 \tag{15}$$

3.7.3 Thermodynamic analysis

Isentropic transformation (H), Gibb’s energy storage separation (G), and saturation enhancement can all be evaluated using the follow - up period (S).

$$\Delta H=E_a-RT_m \tag{16}$$

$$\Delta G=E_a+RT_m \ln\left(\frac{K_B T_m}{hk_0}\right) \tag{17}$$

$$\Delta S=\frac{\Delta H-\Delta G}{T_m} \tag{18}$$

K B=1.38110 [- 22] m2 kg/S [- o2] K (- 1) is the Boltzmann constant, and h=O6.621034 and Planck’s constant IS m2 kg/s, and T m’ is pinnacle’s largest mass catastrophe rate.

Chapter 4-Findings and discussions

4.1 Characterization of material

Dunaliella is the topic of a variety of inquiries, including personal, research, and operational ones. **Error! Reference source not found.** shows proximate, ultimate and chemical composition of quadricauda biomass

4.1 daf basis ultimate and proximate analyses of S. quadricauda

Proximate Analysis (wt.%)				Ultimate Analysis (wt.%, daf)				Chemical Composition (wt.%, daf)				
Moisture	Ash	Volatiles	Fixed Carbon	Carbon	Hydrogen	Nitrogen	Oxygen	Carbohydrates	Protein	Lipids	Others	HHV (MJ/kg)
5.2	4.8	71.3	18.7	47.69	7.11	7.4	37.8	42.1	26.6	19.7	11.6	18.6

DAF: dry ash-free basis

4.1.1 TGA

Figure 4.1 Lubricous change in the process of pyrolysis at 10, 15, 20, and 50 °C/min is depicted as (D)TG bends. There were three distinct areas of degradation. At earlier 200C little components and moisture were eliminated. The dynamic pyrolysis zone, Zone II, had a range of temperature of 200 to 600 °C including all of heating rate. under all amounts of temperature. The substantial mass tragedy of around 76-78 percent occurred at this main temperature. This included disintegration of organic compounds which are non-biodegradable e.g., aliphatic which are saturated, aliphatic amides with long chain, aromatics and also nitriles. Organic compounds were also disintegrated including carboxylic acids and proteins. Also, volatiles were released and tar was formed too by the breakdown of carbon scissions and hydrogen bonds. We can divide this zone into two subzones. When temperature is in the range of 200 t0 400 °C we can find 1st period of this zone and 2nd lasted till temperature of 600 C. Due to degradation of inorganics, there was minor degradation after 2nd section.

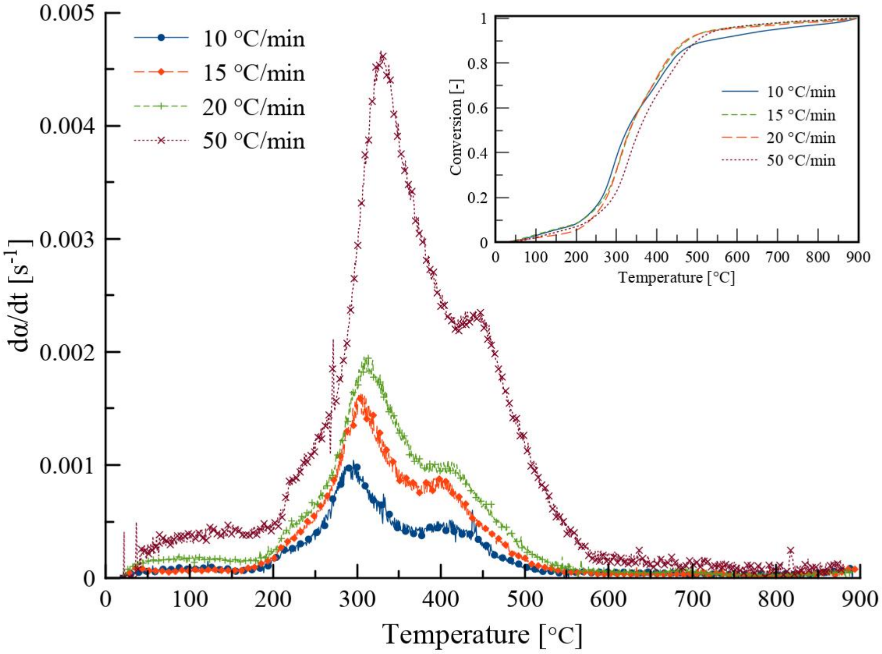


Figure 4.1 Pyrolysis of Dunaliella less to (D)TG curve at various flow speeds

As the growing ratio is increased, the pass rate with the optimal speed changed to a higher temperature. When concentrations of 295.4, 304.4, 308.1, and 328.3 °C were compared, the most intense change rates were 0.001043, 0.001634, 0.001956, and 0.004666 s-1 at 10, 15, 20, and 50 °C/min, respectively. At high temperatures there was delay in thermal degradation when heating rate was increased. For this we can say that when rate of heating is higher for mass and heat transfer time becomes short so volatiles release gets delayed

4.2 Kinetic analysis

4.2.1 Model free kinetic analysis

The active pyrolysis region is of genuine interest through pyrolytic transition, which is why, in the related writing, the majority of the scientists in kinetic analyses do not include devolatilization and evaporation of the components which are known as lighter volatiles and also 3rd section which contains small mass losses is not included. In this work we performed kinetic analysis at .2 to .8 conversion range. Figure 4.2 is representing progression of energy of activation in the 0.2-0.8 range with a 0.01 step size using Greenspan, OFW, and advanced approaches.

Ea increased until it reached a change of 0.6, after which it decreased from 0.6 to 0.8. As Friedman's technique was used, variety in the calculation was important at higher adjustments.

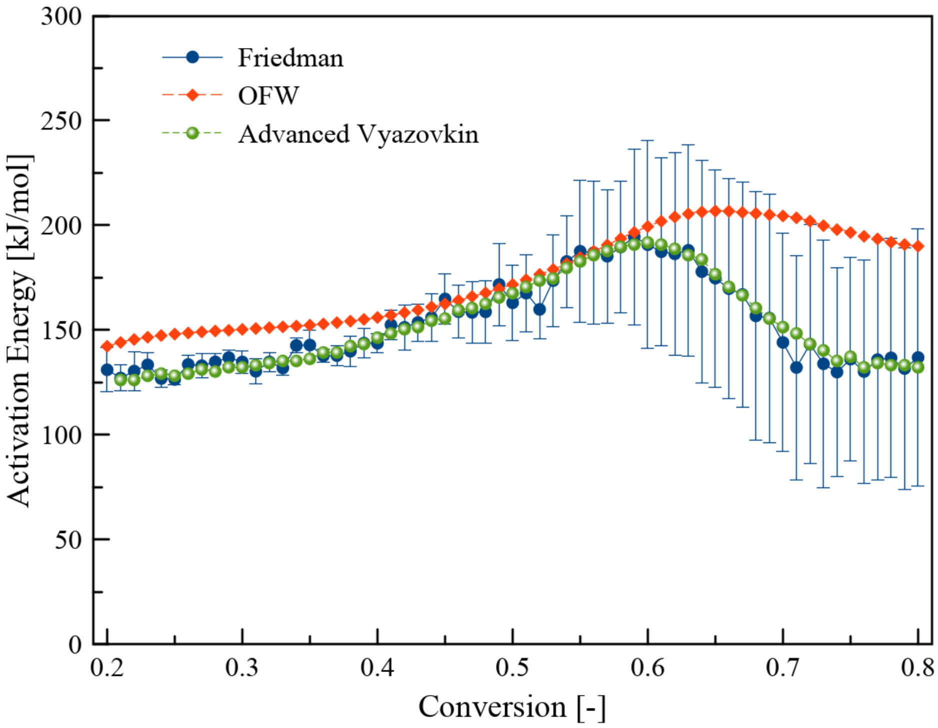


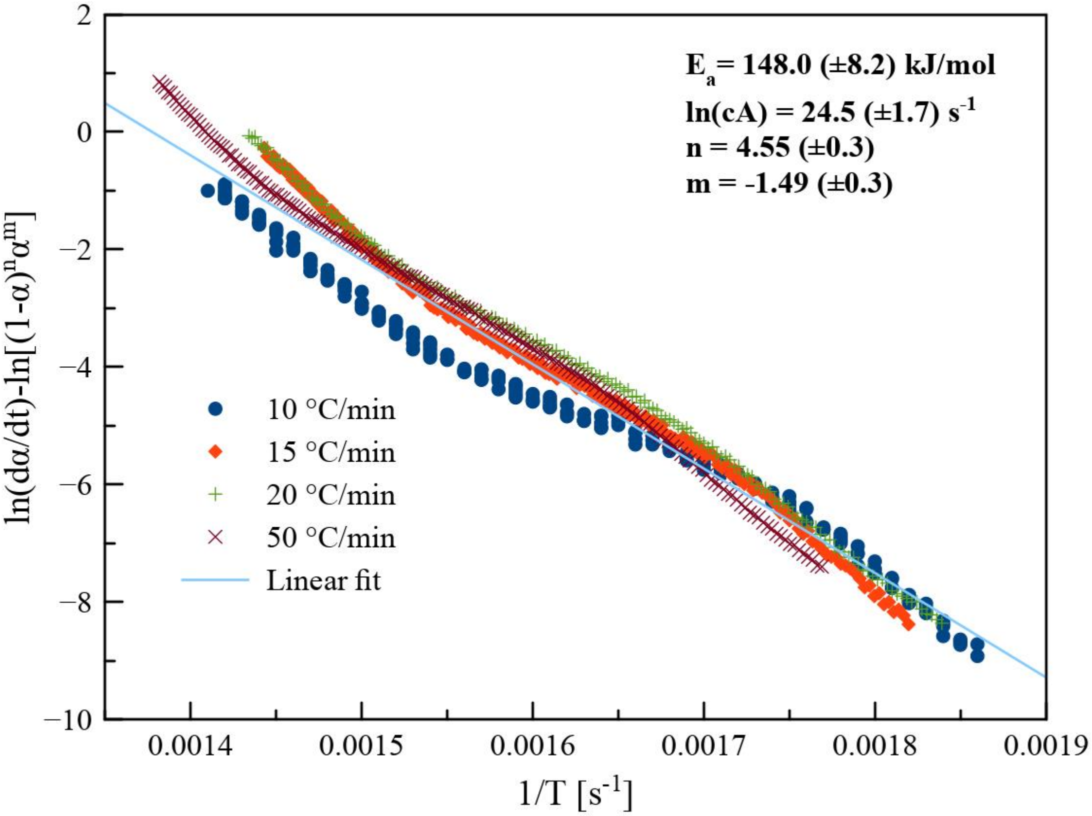
Figure 4.2 To use the inference process, the enthalpy of powerful capacity was profiled.

4.2.2 Model fitting kinetic analysis

To determine involved triplets for a single step reaction Combined kinetic analysis is utilized, the results of optimization are depicted in Figure 4.3(a). In equation six, sets of linear fitting data (10, 15, 20, and 50 °C/min) yielded n=4.55(0.3), m=-1.49(0.30), ln(cA)=24.5(1.70) s-1, and Ea=148.0 (8.1) kJ/mol. In relation to c, the value of A was enormous, so cA could be compared to A, which has a statistical value of 4.36x1010 s-1.

Figure 4.3 (b) represents model functions. These are being drawn against 5 near mechanisms of reaction.

(a)



(b)

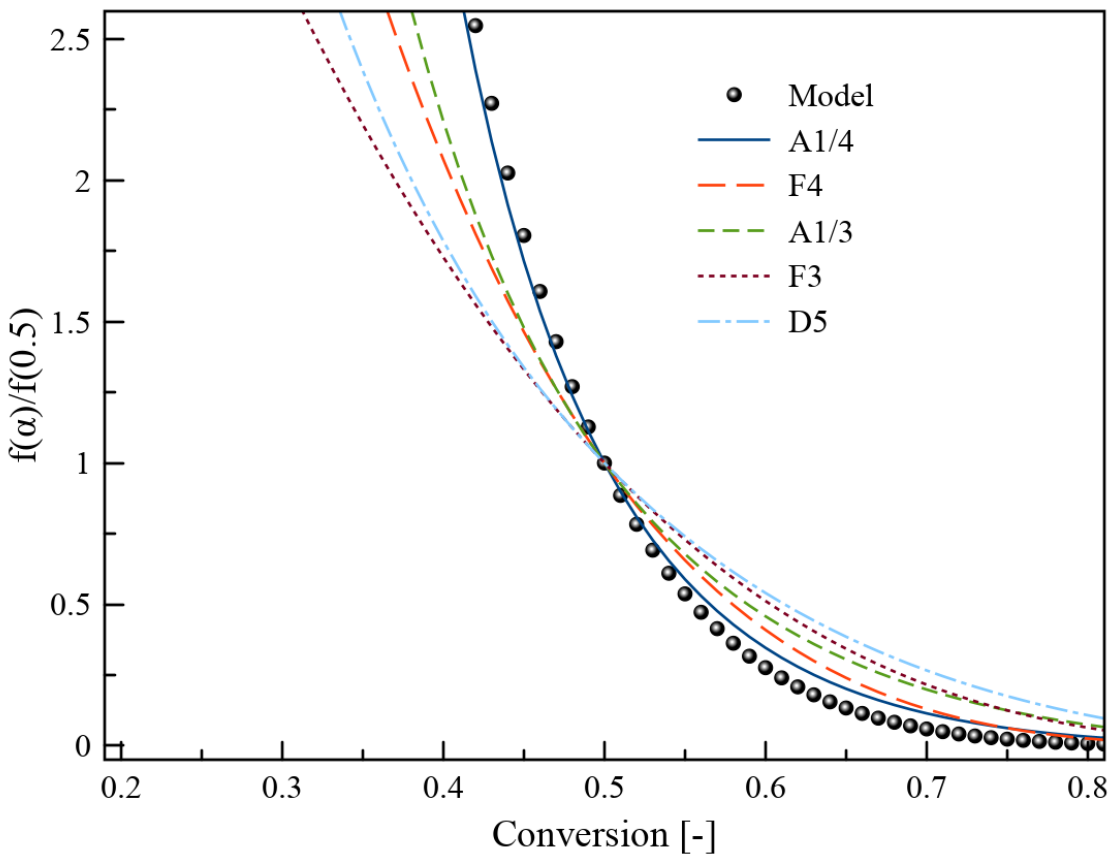
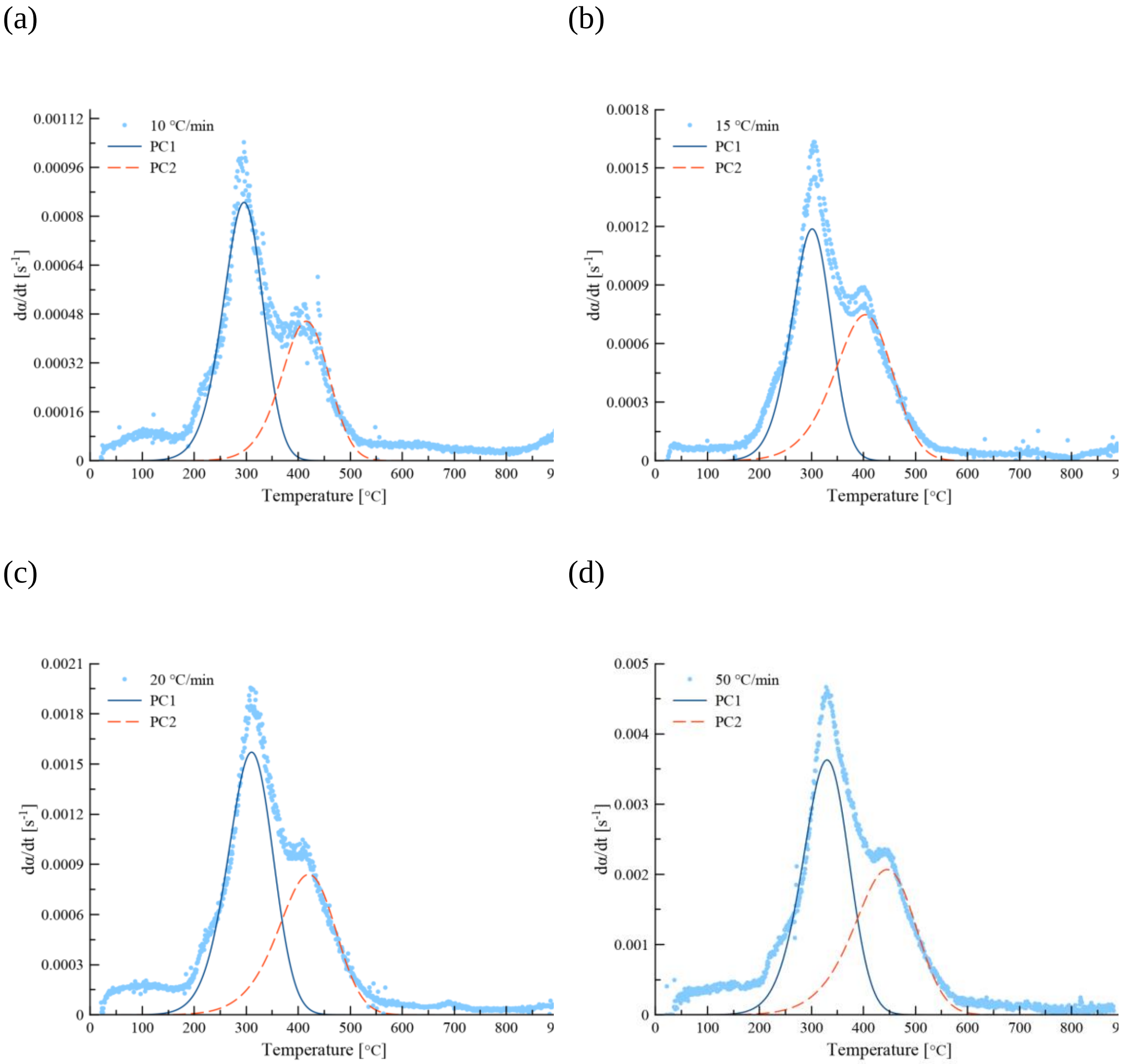


Figure 4.3 Integrated isotopes (a) refinement effects and (b) system alignment against 5 nearby frameworks in the pathway of 0.2-0.8

Taking single reaction, in the range of 0.2-0.8 of conversion A1/4, an Avrami-Erofeev's equation are mechanisms of reaction. diffusion was controlled with geometry mechanism which was contracting and it had Avrami-Erofeev's exponent value <1. But there was complex degradation considering profile of activation energy so it requires more elaboration.

4.3 Independent reactions in parallel

In the dynamic pyrolysis field, two separate equal responses were assumed, as shown in Figure 4.4, and the structured limits were relinquished.



(a)

(b)

(c)

(d)

Figure 4.4 Installation of difference between the two models at 10°C/min, 15°C/min, 20°C/min, and 50°C/min.

Carbs imploded between 200 and 350 °C during pyrolysis, proteins were degraded between 220 to300 C, and lipids between 270 and 580C [11–14]. So, we can say that Pc1 relates to the low temperature decomposition of components which are thermally stable in proteins and carbohydrates and pc2 tells about decomposition of thermostable component at higher temperature including lipids and others. In **Error! Reference source not found.** optimum kinetics for pseudo components are shown

4.2 For 2 pseudo components optimum kinetics

Heating rate [C/min]	Pseudo component 1					Pseudo component 2					SSE (1/S^2)	Fit (%)
	E (KJ/mol)	A (1/S)	M	n.	P	E (kJ/mol.)	A (1/s)	M	n.	P		
10.0	79.980	5.23E4	O	1.36	0	100.00	5.14E4	O	1.43	O	1.3E-7	99.67
15.0	80.690	7.22E4	O	1.54	O	63.79	1.15E2	O	1.17	O	1.4E-7	99.14
20.0	73.800	1.84E4	O	1.57	0	65.89	1.59E2	O	1.16	O	1.6E-7	99.28
50.0	77.320	5.19E4	O	1.60	O	63.0	1.50E2	O	1.07	O	8.1E-7	99.32

PC1 had a normal manifestation energy of 77.95 (3.12) kJ/mol, a post factor of 4.86E4 (2.24E4) s-1, and n=1.51 (0.10), while PC2 had a normal enactment energy of 73.26 (17.93) kJ/mol, a well before factor of 1.32E3 (2.611E3) s-1, and n=1.21

As seen in, reproduction using significant bivariate distinctions reveals solid match at different shaping speeds. Figure 4.5

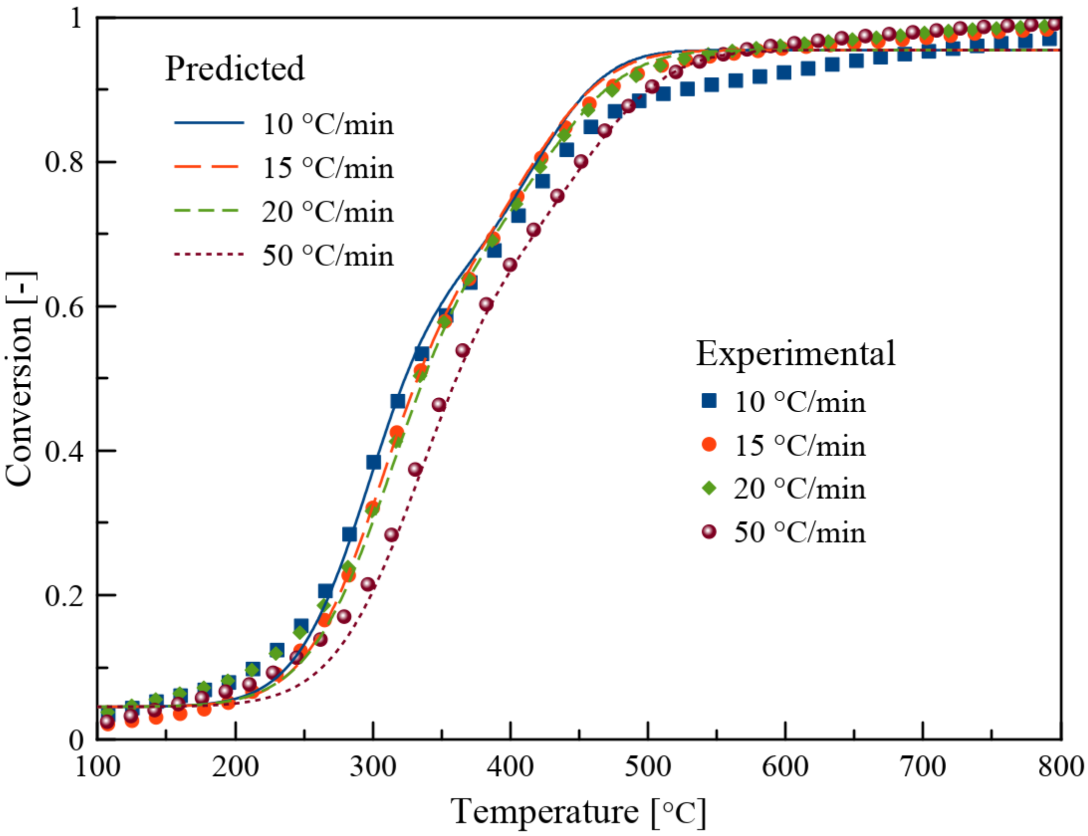


Figure 4.5 Thermodynamic analysis

4.4 Thermodynamic analysis

Conversion of S. quadricauda giving f ΔH, ΔG, and ΔS through pyrolysis by thermodynamic analysis is shown in Table. Change in enthalpy and change in gibs free energy are +ve for Pc1 and Pc2. So, it tells that to carry out both reactions external energy source is needed. It was concluded that at higher heating rates difference b/w activation energy and enthalpy change increases for both of reactions. PC1 had a mathematical difference of under 5.07 kJ/mol, while PC2 had a mathematical difference of under 6.05 kJ/mol, little work was needed to create activated complexes for both of reactions. We obtained -ve values of change of entropy for both reactions so it tells us that products from both reactions are stable. So, we can say that conversion of S. quadricauda is thermally suitable.

4.3 Thermodynamic parameters

Heating Rate (C/min)	T_m (K)	ΔH [kJ/mol]	ΔG [kJ/mol]	ΔS [kJ/mol K]
	Pseudo Component 1 (Conversion at low temperature)			
10.0	569.429	75.255	171.170	-0.1680
15.0	575.577	75.896	171.253	-0.1660
20.0	585.222	68.938	172.687	-0.1770
50.0	608.900	72.269	175.118	-0.1690
	Pseudo component 2 (Conversion at high temperature)			
10.0	689.595	94.364	211.611	-0.1700
15.0	678.194	58.149	207.278	-0.2200
20.0	695.722	60.099	212.290	-0.2190
50.0	726.521	57.540	216.286	-0.2190

Conclusions

Microalgae S. quadricuda’s Valorization during pyrolysis was delve into by the use of thermodynamic and kinetic analysis. In the line of conversion Ea in model free manner was estimated by OFW & friedman & advance Vyazovkin’s techniques. From master plot it was found that reaction of Avrami-Erofeev’s A1/4 had most likely single step mechanism. Reaction model was found through linearization of rate equation via joined kinetics and reaction was considered single step. Despite in passive reaction zone profile of Ea showed two reaction degradation. For low temperature mean activation E recorded is 77.950 (±3.120) kJmol−1. While 4.86E4(±2.240E4) s-1 is the value of pre-exponential factor and the value of n is 1.510(±0.100). The second reaction was carried at higher temperature, the mean activation E obtained was 73.260(±17.930) KJ/mol with 1.32E3(±2.610E3) s-1 pre-exponential coefficient and value of n is obtained as 1.210(±0.160). The study involving thermodynamic parameters as entropy, Gibbs free energy and enthalpy during pyrolysis it was concluded that reactions become more favorable when little more energy is provided in place of enthalpy.

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