Thermochemical decomposition of tannery sewage sludge in air and nitrogen environment.

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Dedication

By the grace of Almighty Allah, who is the most Beneficent and the most merciful

This research is dedicated to my parents, who have always been my source of guidance and support.

To my supervisor who shared his knowledge, gave advice, and encouraged me to fulfill my tasks.

And to all my fellows, with whom I worked with and shared good memories.

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All praises to Almighty Allah, without His will nothing can happen, who favored us with the capacity to think and made us anxious to investigate this entire universe. Incalculable greetings upon the Holy Prophet Hazrat Muhammad (PBUH), the reason for the creation of the universe and wellspring of information and blessing for whole humankind.

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Arslan Khan

Abstract

The disposal and the management of sewage sludge from tanneries is a challenging issue for the leather industries because of their adverse effect on the environment. This study describes the detailed characteristics and assessment using thermodynamic and kinetic parameters of the tannery sewage sludge conversion in air and nitrogen. Isoconversional model-free methods like Flynn-Wall-Ozawa (FWO), Friedman and Kissinger-Akahira-Sunose (KAS) were employed to investigate the kinetics and the thermodynamic parameters in the air environment. E_a for the Friedman, KAS and FWO were investigated in the study. The curves of DTG at 5, 10, 20 and 40 °C/min shows that the conversion can be divided into three major stages. Along with that, this study also investigates the frequency distribution by applying the DAEM model. There are six pseudo-components involved in the frequency distribution of the air environment while the seven pseudo components involve in the pyrolysis of tannery sewage sludge. For the thermal degradation prediction of the sewage sludge from the tannery, an artificial neural network (ANN) of the MLP-3-7-1 and MLP-3-11-1 model were used for the combustion and pyrolysis. Ea values for the model ranges are Friedman(148.96kJ/mol-395.23kJ/mol), KAS(169.65kJ/mol-383.75 kJ/mol) and OFW (176.44kJ/mol-377.85kJ/mol). Furthermore, the values of ΔH, ΔG, and ΔS are also in good agreement. The negative values of the entropy changes show that they are in good agreement. The model shows that there is a good agreement between the experimental and the predicted values. Overall, this study develops the importance of the ANN model which should be utilized as a suitable model to fit experimental data of thermogravimetric analysis.

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Acronym

DTG	Differential thermogravimetric analysis
FTIR	Fourier transform infrared spectroscopy
TSS	Tannery Sewage sludge
SEM	Scanning Electron Microscope
EDX	Energy-dispersive-Xray spectroscopy
Ea	Activation Energy
TGA	Thermogravimetric analysis
ANN	Artificial Neural Network
DAEM	Distribution Activation Energy Model

Chapter 1

Introduction

1.1 Background

The growing population and the demands of energy have an adverse impact on the environment. Modern industry is capable of fulfilling the needs of this ever-rising population. Industrial operations are a major threat to the existing environment and biodiversity. Considering the nature of the effluents that are released into the environment every day, one million tons of waste per country is also being generated around the major populations of South Asia. This scenario requires the emphasis on the various sustainable development goals which can objectively determine the future of biodiversity[1]. A massive amount of non-recyclable waste from the leather industry is produced every day[2]. Most solid waste is not recycled effectively and instead of this dumped in landfills. The tanning industry is basically known as a pollution-intensive industry. It generates approximately about 4 million tons of solid waste per capita around the world[3]. Many of the operations in the leather industry are performed in the water. Therefore, wastewater effluents are one of the main problems in the leather industry and surely need to be well treated. Approximately 0.2 kg of sludge (dry basis) have been reported to be generated as a result of wastewater treatment[4]. From the initial treatment stages, the sludge is generated by the complete treatment of the wastewater or the wastewater treatment plant. For the disposal of tannery sewage sludge, various options are in place, including landfilling, anaerobic digestion, agricultural use, and incineration[5]. Some of the options from these will not be available in the future and require further pretreatment steps. Due to this strict criterion, waste disposal requires efficient recycling of resources without harmful supply of substances. Thus, industries have started to consider waste recycling and the use of waste both for recycling and for both economic and environmental concern. Chemical methods of obtaining valuable products are a desirable approach in modern times. It is related to the nature of the products and the abundance of the resource, and the fixation of the waste, which is a serious threat to the environment. The leather industry is an important part of the industrial growth of any country. The leather product is very significant and has a history of contributing to the industry's economy. Leather goods and footwear industry has a worth of more than 215 billion dollars in the global market. To deal with the limited natural resources, the circular economy deals like a 4R policy which is reduced, reuse, recycle and the recovery can motivate the various enterprises to reuse particular things, recycle the thrash and reduce resources consumption. The concept of a close loop supply chain (CLSC) can potentially avoid environmental contamination.

1.2 Tannery effluents:

During the leather processing different types of pollutant are generated. It can be seen from the literature that only 25% skin or the raw hide is processed to form the leather. But to some extent it depends on the animal species its exact percentage depends on that are the specification of the products. That is why the rest of the weight and the chemicals that are processed and unused is discharged in the wastewater that leads towards the residue in the process at some point. From the tannery industry the residues can be certainly classified as by-products, hazardous waste, and the nonhazardous waste [6]. Among all the industrial waste generated the tannery effluents of the tannery are the highest pollutant producing industry [7]. The effluents produced from the tannery industry are complex by nature and that certainly have the characteristics which depends on the processes. The pollutants of the tannery industry are highly organic and the inorganic in nature. The consumption of chemical reagent is very high in nature. Majority of these chemical is discharge into the effluents because majority of the effluents are not going to absorbed during the whole process. About 45-50 m^3 of the wastewater is being discharged for one tone of the raw ride that is processed[8]. The whole process of the tanning is certainly accompanied by surely consumption of the large volumes of the water. The pollution load that is discharge into the effluents which includes the chemical oxygen demand (COD), biological oxygen demand (BOD), Sulphides total solids and the sludges. [9]. It is somehow observed that during the wet processing stages of the leather industry wastewater occurs which includes tanning and the retaining processes and the beam house. The above-mentioned stages include the total pollution load of 90%. The residue of the wastewater is called as the sludge which somehow deposits as the high-water content silt on the settling tank bottom.

Tannery industry mostly produced the large amount of sludge that contains the calcium, nitrogen, magnesium, phosphorous chromium, and the certain amount of sodium as well. The enhanced concentration of the trivalent chromium with the organic and inorganic compounds in the leather industry sludge might be a source of the ground water contamination. It is somehow quite interesting to recover the chromium from the leather sludge. Different solid wastes produced from the tannery are present in Fig.1

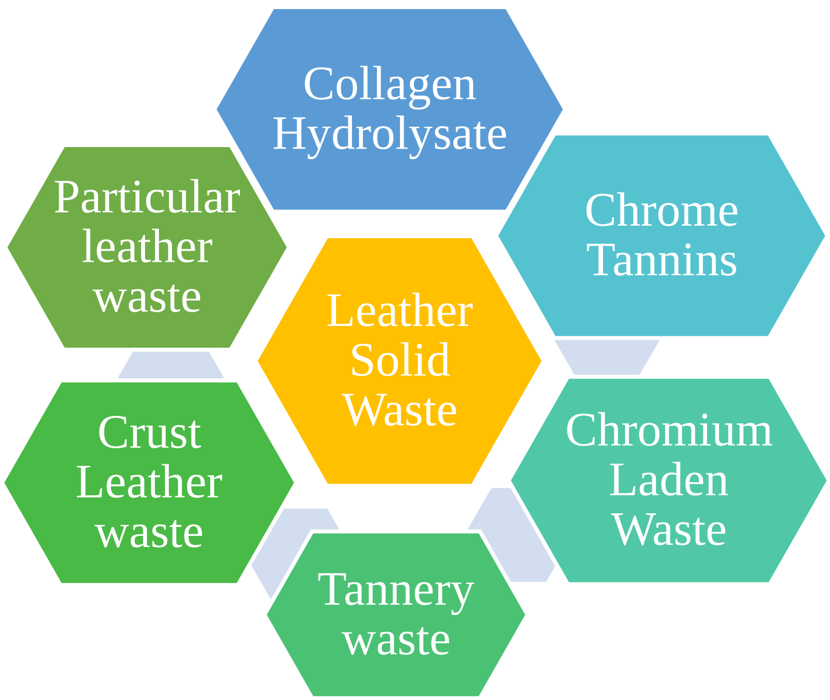


Fig. 1: Types of Different types of solid waste from the leather industry

1.3 Tannery sludge:

Leather industry is the major sources of pollution and tannery wastewater is environmental concern. Serious environmental impact is being imposed by the tannery sludge(with its, discolouration, high oxygen demand and toxic chemical constituents), atmospheric and the terrestrial system. Tannery sludge contains both organic and the inorganic pollutants. The organic pollutants that certainly comes from the hides washing include proteins, carbohydrates and lipids. The inorganic pollutants are different solvents, additives and the chromium that comes from the chemical added in different processes of treatment. The hazardous element that is formed during tanning operation is chromium (VI) which is oxidized from chromium (III). As it is carcinogenic and mutagenic in the form of Chromium (VI) it can cause allergy. Based on the literature the permissible level in the industry for chromium is 3mg/kg.

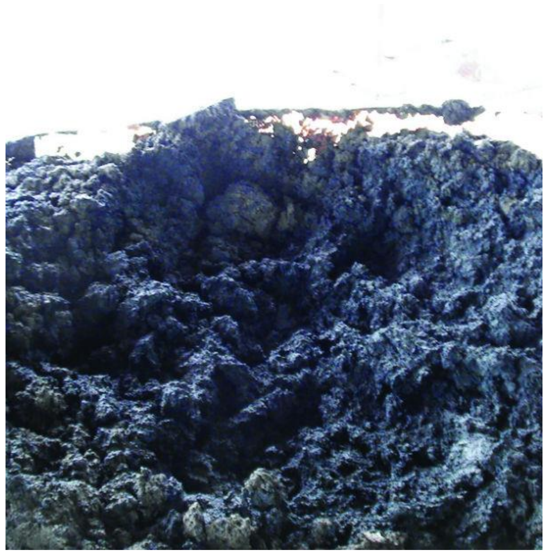


Fig. 2: Tannery sewage sludge

1.4 Mechanism of combustion and pyrolysis

1.4.1 Combustion

Combustion is a

- Exothermic Process
- React with Oxygen
- Heat is evolved

Tannery Sewage Sludge + Oxygen → Heat

It certainly depicts the phenomena with the various applications in the industry, different professions, and the sciences. In simple we can say that it is the most chemical reaction and surely considered an important step for the oxidation of different kinds of substances.

1.4.2 Pyrolysis

Pyrolysis process starts with the formation of vapors of volatiles, then it destined into valuable products (Biofuel, petrochemicals etc.) by the deprivation of non-volatiles. Then with the increasing temperature hydrocarbons and benzene derivatives in the gaseous form are produced by the secondary decomposition of char. The solid degradation of the mechanism of pyrolysis are presented in the Fig. 3.

With the temperature increase, the fuel gas having higher percentage of hydrogen produces because dehydrogenation reactions de-carbonization of oxygenated hydrocarbons can increase in H_2 that comes from substantial hydrocarbon compounds. Furthermore, H_2 can be act as upright pointer for the secondary cracking of tars to reduce the amount of it.

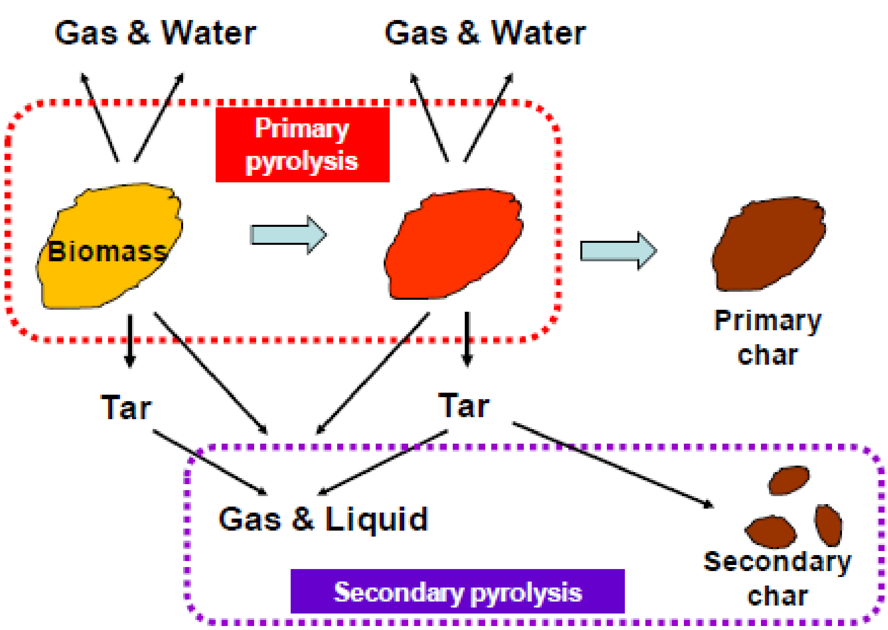


Fig.3:Mechanism of solid degradation reaction in a pyrolysis process

It is concluded that CO and CO2 produce at the temperature range of below 450°C due to the breakage of carboxyl and carbonyl functional groups of RH. CO is the main secondary product produced at elevated temperature due to the cracking reaction. Moreover, hydrocarbons also degrade at high temperatures, that can be illustrated in reaction below:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$C_2H_4 \rightarrow CH_4 + C$$

It is estimated from the previous findings of the author that thermochemical treatment by pyrolysis can enhanced the saving of tannery (about million dollar per year) by recovering of the chromium compound and the energy. In comparison of the combustion, the process of pyrolysis is highly dependent on the various combustion which include temperature and the different heating rates, With the pyrolysis it yields high energy gaseous and the liquid products which is somehow certainly used as the fuel[10] . The pyrolysis final temperature signifies the ratios of gas liquid and the solid products. At the lower temperature certainly below than 450ºC the highest portion of the solid waste is obtained which signifies that the incomplete decomposition of the organic matter.in thermal processes chromium is bound to the solid phase that somehow can be disposed off safely. There is a risk of converting the Cr (III) to toxic Cr (VI) at the higher temperature during the combustion process. So, it is important that at the higher temperature with the presence of the some of the oxidizing agents the chromium will somehow change it oxidation state to the Cr (VI). Care must be taken to ensure that pyrolysis must be done at the lower temperature typically between <600 ºC to avoid this oxidation state transformation[10].

1.5 Problem statement

- Leather industry produces massive organic and inorganic sewage sludge. Volume and the nature of this sludge requires a solution for sustainable conversion of this waste to energy.
- Credible energy potential analysis of this organic sludge is imperative in order to formulate a bench scale conversion process.

1.6 Research Objectives

To overcome the existing challenges in thermal degradation behaviour of the tannery sludge, following objectives were identified.

- To prepare and characterize samples of sewage sludge for combustion and pyrolytic applications.

- To investigate the insight of kinetics and thermodynamic parameters of the tannery sewage sludge in both oxidative and nitrogen environment
- To study and compare the experimental and predicted values of Ea by the application of Artificial Neural Network Modelling (ANN) in air and nitrogen environment

1.7 Scope of Study

The following scope was established to ensure that the research would be carried out in the time available:

- Combustion and pyrolysis of the tannery sewage sludge by TGA is one of the considerable ways to address the research hotspot.
- To demonstrate the detailed approximation of kinetic and thermodynamic parameters that is vital for considerate and the artificial neural network modelling of both the combustion and pyrolysis process. This work has comprehended resolution to interpret a detail description of sample preparation, characterizations (FTIR, SEM and EDX),
- The Model Free method was used by consolidating different models, including Friedman, KAS and OFW method. The best-fit model was subjected used to study the kinetic results.
- To compare the experimental and the predicted values of activation energy by the application of artificial neural network (ANN) in this study.

1.8 Chapter Summary

This thesis comprises of five chapters. The exposure of each chapter is given in the following chapters.

- **Chapter 1** delivers vision of the subject, background and contemporary problems related to the work. It also clarifies the problem statement, research objectives and scope of the planned study.
- **Chapter 2** will sketch the literature review achieved to describe the previous work done on the thermochemical conversion of different tannery waste. It also includes

review based on solid waste from the leather industry and their valorization method.

- **Chapter 3** covers the methodology related to the sample preparation and characterization. Combustion and the pyrolysis study of the sludge and thermokinetics analysis by the model free approach.
- **Chapter 4** delivers results and discussions. The material characterization, experimental, kinetic and thermodynamic and the modelling to compare the experimental and the predicted values and its consequences are existed and explained based on various point of view.
- **Chapter 5** reviews all the findings and conclusions in the current study and provides the future recommendation for the related work.

Chapter 2

Literature Review

2.1 Literature review

The making of leather is the somehow traditional also the important industrial sector that certainly gives the different qualities of the leather and the leather products [11-14]. Due to the enhanced demand for leather goods globally, the tannery industry growth rate is increased rapidly. The tannery industry is basically the resource-consuming sectors along with the most polluting industry.

The range of products which are produced in the industry refer to the pollutants and effluents. Organic and inorganic entities pose a major threat to the environment. Major developments related to the waste fixing are required are at industrial scale for proper solutions. Industrial sludge is one of the fixations which needs to be on top, while addressing the environmental issues. Focusing the problem such solutions are imperative to be coined, which pose minimum energy requirements and threats to the environment.

Tannery sewage sludge has bacterial and pathogen growth which creates the necessary carbon in the mass. This can be successfully implemented in order to produce the necessary fuel which can be employed for further useful purposes.

According to the statistics, 0.25Mg of the leather is produced from 1Mg of the input raw material and it certainly requires 15000m^3- 120,000 m^3 of water finally generates about the 15-50 Mg the water being waste and approximately 40-700kg of the solid waste [15]. Along with the wastewater and the solid waste the processing of leather also produces the gaseous waste which certainly leads to the greenhouse gases (CO_2, H_2S, NH_3) and the organic compounds that are volatile in nature which include the aldehydes, hydrocarbons, and the amines. The leather itself is being covered and dyed containing some sort of pigments which include metals and also the resin. The chromium amount that is being calculated is as Cr_2O_3 in the finished leather goods that somehow reach up to the 4 % of the dry mass and the amount of the highly toxic chrome Cr (VI) can also be well over 50 mg/kg [16, 17], the amount of Sulphur can also exceed to 2.5% in the leather and its value exceeds to the 4-5% in furs. In the majority of the locations the water that is waste is dumped and it is not treated adequately. As we know that the leather industry plays a vital role in the economy of the many industries and somehow it is an important concern of the world meat chain, and it is also important to reduce the negative impact on the industry and the environment. The type of treatment technology being adopted to process the leather vary significantly and the chemicals emitted from that also depend on the technology of treatment [18]. In the tannery industry, over 4 million tons of solid waste associated with the leather are being produced every year [19]. Since the different traditional method that is being adopted would cause environmental pollution [20]. Although it has been observed from the literature these solid leather waste somehow contains a lot of protein which could be a very valuable resource in the different fields [21]Various attempts have been made in solving this waste problem and converting this into useful products [10] but the implication and the cost certainly results in a lack of acceptance method. Three different challenges that the leather industry is facing in the context of the circular economy. Water should be utilized in closed cycles with the sedimentation and the clarification and removal of salts with the help of reverse osmosis. On the other hand, the energy that is being used in the leather industry and drying during production must also be recovered. Finally, the amount of chromium that is present both in the final products and the waste needs to recover and reuse. This study focuses on the result obtained from the different thermochemical conversion methods, which include pyrolysis and gasification. Also, some of the dechroming techniques from the chrome tanned leather waste are examined and their maturity level in terms of technology readiness level is evaluated. The concept of sustainable energy development and the circular economy concept involves the cyclic materials flow and the energy involves in that mainly focus on the upgrading [22], in other words, means that the reuse of waste as the raw materials. The primarily concept of circular economy is the more economical than some traditional economic model and it is also more beneficial for the environmental perspective as well. This circular economy concept surely enhances the development of the various enterprises by the introduction of the technologies for the improvement of their goodwill [23]. The leather industry poses some serious environmental issues as well so the safe disposal of the waste from the tannery is also examined in this study. The focus of the review paper was to show the sustainable technological solutions by thermochemical conversion which involves the gasification and the pyrolysis to convert the tannery waste into useful products. the growing concern about the quantity of waste and the raw material utilization meant that many of the entrepreneurs would have to be faced the challenge of the reconciling the needs of the consumers with the proper management of waste, which surely requires the more research for the leather industry waste treatment for information in context to get the waste properly to the market.

2.2 Solid waste

Enormous amount of leather waste is produced in the tannery industry which includes the solid waste. In addition to those environmental concerns of the discharge and the landfill costs can cause a serious problem for their management alternatives and the industry about the overall consideration have surely been based on the multisport[24]. At the different stages of the leather industry huge amount of the solid waste are produced during the processing of leather and no specific adopted method is available for the solid wastes that is generated from the leather industry. The leather solid waste mostly produced in fleshing operation, trimming, shaving process and the splitting and in addition to that sludges discharge from treatment plant that can contribute to increase the large volume of wastes[25]. Specifically, out of 1000kg of the raw hide, 800 kg of the solid waste are generated in the manufacturing of the leather and only 200kg is converted into valuable products. There is about 600000 tons of the solid waste is generated from the leather industries annually [26]. In the subsequent Fig.4 the different types and the quantities of the solid waste that is generated in the leather manufacturing industry based on 1 ton of the raw hide skin. From the tanning industry the characterization of the solid waste is well known. For every type of leather waste that are generated have the different characteristics as well. To find out the applications of different wastes it is somehow very important to find out the exact nature of the waste. In addition to that some of the solid waste contain chromium and certainly be categorized as the waste hazardous in nature. So, it must be noted that a safe disposal needs to be ensured.

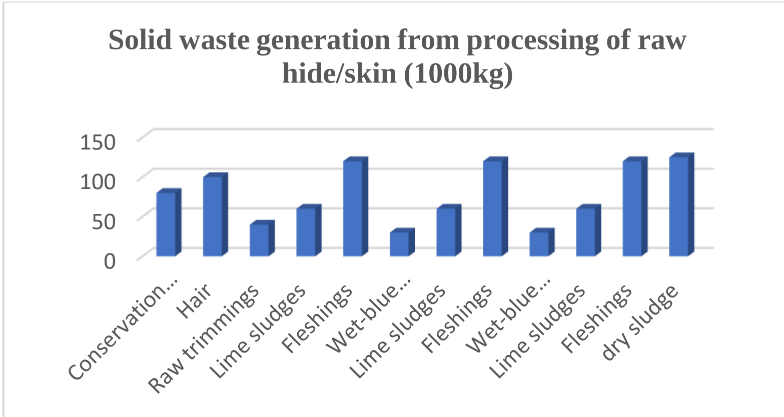


Fig. 4: Solid waste generation from one ton of raw hide skin

The waste that are being generated during the leather processing are the splitting, trimming, fleshing and shaving processes and the sludge that is also generated in the wastewater treatment plant that contributes to the waste increase [25]. Various ways to valorizations and the disposals of these wastes are specifically be drawn by that kind of wastes that surely depends on the fact these solid wastes are produced in the beamhouse in the tanning and after tanning. These wastes differentiation is called as the untanned and the tanned waste.

2.3 Types of solid waste

The type of solid waste that is obtained during the different processing stages are given under:

- Untanned wastes
- Tanned wastes
- Chromium tanned solid waste

2.3.1 Untanned wastes

The untanned solid waste is due to biological degradation of rawhide that creates the handling and transport problems and discharge difficulties in the landfill would also occur. In the beam house section during the fleshing operation large amount of solid wastes generated. This solid waste is called as fleshing waste. The mechanical process of fleshing basically for the deposit's removal of the flesh or skin fats from inner parts. This mechanical process aims to remove the flesh deposits or the fats from the skin inner parts [27]. Subcutaneous tissue, flesh and fat, that is composed of the protein (5-7%), fat (4-18%), Sulphides (2-4%), lime (2-6%). [27].

Just after the completion of fleshing operation, trimming is to surely the cut out of the parts of the skin/hide that is being processed. Cut-outs of the operation is called as the trimming and might be transported and being shipped to the glue manufacturers and other by-product manufacturers and then sent in the landfill for the disposal[28].

These untanned wastes from the solid includes the various leftovers from the trimming of the raw hide and the surplus parts after the fleshing and the liming and mainly composed of the large amount of grease and collagen. These solid wastes chemical composition mainly depends on the quality and the type of the raw hide and the operating conditions. Proteins and the fats are the main components of these wastes (10.5%). The amount of moisture is 60%. The solid wastes from the leather industry certainly do not contain the compound of chromium [29]. The residue of grease and the oils can somehow also be used to extract the oils and the fats, which is surely be used as the raw material for the biofuel and the leather fat liquor [30].

2.3.2 Tanned wastes:

The tanned solid waste produced from the leather industry poses a serious problem in handling this waste. Waste obtained from chromium-tanned leather basically consists of protein and chromium. The stability of the material is certainly the output of the complexion between the salts and the chromium (iii) and the carboxyl groups of the certain collagen. That tanned solid waste includes [31, 32] the buffing dust generated after the treatment of the leather surface. Chromium-containing solid wastes which is known as tanned wastes is basically the wet blue shavings, finished leather trimmings, buffing dust and leather industry sludge from the wastewater treatment. [33]. Composition of these wastes comprises of oils and fats(3-6%), and the composition of the mineral matters about

15%. Worldwide, chromium is widely used they typically contain about 3.5% to 4.5% of the chromium in the form of Cr_2O_3. Tannery sewage sludge from the tannery effluent mostly contains water which is about 65%, chromium III around 2.5% and the organic substances 30% [29, 34].

During the machine process chrome shavings wastes are generated. Shavings are specifically the scarps from the leather flesh sides which is typically carried out by leather cutting of the unusable parts and the different rags which is created during the shaving operation [35]. Safe disposal of shavings and its utilization have put the various problems in many ways and somehow this is more critical because of their consumption. Approximately 95 to 100kg of wet blue shavings are produced by one ton of raw hide processed[36, 37]. Tanned splits are also the tanned waste from the leather industry. By splitting the leather horizontally, the pats we get (flesh splits) somehow correspond to the flesh side of the leather, along with that trimming waste also generated which is obtained from the different operations of the finished leather, these wastes are called the trimming waste.

2.3.3 Chromium tanned solid waste

By cross-linkage chromium ions to the free carboxyl group in the part of collagen by which chromium tanning is based tanning . This chrome-tanned leather is known as the wet blue leather, and it is characterized by handling quality and its versatility [38] almost 60-75% of chrome gives Cr_2O_3 that surely remains in the collagen structure at the end of chrome tanning process. Trivalent chromium oxidation into the hexavalent form causes serious impact on the environment, because is toxic in nature. When the leakage of chromium occurs, it can cause contamination of groundwater. Pollution due to water affects aquatic life, and the soil contamination imposes different health effects and poses serious health hazards by the toxic dust inhalation by both livestock and the people[39]. The different types of solid wastes that is produced in the leather industry are illustrated in Fig. 5.

Fig.5: Types of leather solid waste

2.4 Characteristics of tannery industry solid waste:

From the literature study the characteristics of different solid waste including splits, offcuts, shavings, hair and birse and the fleshing waste are given and along with that the wastewater treatment effluents including the sludge are also given in Table.1:

Table 1: Characteristics of tannery industry waste

No	Waste	Definition	Production	Component(valuable)	Component (Risk)	Valorization	Potential	References

						methods	**product of valorization.**	
1	Tannery sludge	Solid waste from wastewater and effluents treatment	8.5-12kg per m^3 of the treated wastewater.	Mg, Ca	Organic compounds, dyes, Cr, pathogenic microorganisms	Incineration, leaching, hydrolysis, landfill disposal.	Ash	[40]
2	Split and offcuts	Leather processing unusable solid waste (shaping, cutting)	4.3-.5 kg per 1Mg of processed leather	Fats, protein	Compounds of organic, dyes, tanning agents, Cr	Incineration, Hydrolysis, digestion	collagen, hydrolysis ash, active carbon	[41]
3	Shavings	Trimming solid waste and leather shaping process	100kg per 1Mg of leather processed	Collagens	Cr, dyes, tanning agents.	Alkaline hydrolysis.	Collagen protein as hydrolysis with low percentage of residual	[42]

							chromium	
4	Leather dust	Fined powder of collagenous fibrils being dangerous solid waste generated via leather buffing (carcinogenic properties)	2-6kg per 1Mg of processed leather	Collagens	Cr, dyes, Synthetic fats and the tanning agents	Incineration, hydrolysis, anaerobic digestion	Activated carbon, hydrolysis of collage.	[43]
5	Fleshing waste	Residue wastes from the tanning of raw hides which is originated by the removal of tissue.	50kg per 1Mg of processed skin	Proteins and the fats	sodium chloride and the tanning agents.	Hydrolysis, incineration, fat extraction	Soap, protein hydrolysis biodiesel.	[44]

6	Birse and the hairs	At the hair pulping process the solid wastes obtained	3.5 kg per 1Mg of processed skin	Keratins	---	Hydrolysis, incineration, landfill, disposal.	Keratin hydrolysis ash, activated carbon	[45]

Chapter 3

Materials and Methods

3.1 Raw material

Sewage sludge from the tannery was obtained from Siddiq Leather Works (Pvt), Lahore, Pakistan, for this research work. Tannery sewage sludge was first sun dried and then in oven at temperature of 105°C for 24hrs to remove the inbound moisture content. The dried sample is then crushed and ground on the Hardgrove Grindability Index Tester (USA) to generate a 0.23mm particle size by sieving (RX-29-10, WS Tyler).

Fig.6:Schematic of sample preparation of tannery sewage sludge

3.2 Thermogravimetric analysis

For the combustion environment tests of TGA were done by use of thermogravimetric analyzer. 5-6 mg of samples was put into the crucible of ceramic and heated from ambient temperature to 800 °C. The experiments were being performed at the four heating rates which includes 5, 10, 20, 40 °C/min. To ensure maximum precision of the results, all the experiments were repeated three times.

3.3 Kinetic analysis of tannery sewage sludge combustion

To study the thermal reactivity of the raw material TGA is widely used. Kinetic analysis is an effective method to examine the materials thermal stability in combustion. The conversion rate of a solid material are derived from the following equation[46].

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

where α be the conversion degree during the combustion , the rate of conversion in the equation is denoted by $d\alpha/dt$, t is the time while the absolute temperature is T,

From the equation given below, α can be calculated

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \tag{2}$$

where initial mass of the sample is denoted by m_i , m_f is the sample mass when the reaction ends and m_a is certainly mass of the sample at time "t" during the combustion reaction. Kinetic parameters are estimated from the mass-dependent difference in the degradation rate during heating. At any temperature, the rate constant can be elaborated by the Arrhenius equation.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

In equation (3),the pre-exponential factor is denoted by A, while the activation energy of the reaction is E_a. R is the universal gas constant that is equal to 8.314 J/mol. K, while the absolute temperature is T.

Substituting Eq. (3) in Eq. (1)

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \tag{4}$$

With an increase of temperature at a constant heating rate,

$$\beta = \frac{dT}{dt} = \frac{dT}{d\alpha} \times \frac{d\alpha}{dt} \tag{5}$$

Substituting equation (7) into equation (6) and integrating

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T} \exp\left(\frac{-E_a}{RT}\right) dT \quad (6)$$

Where the integral function of conversion is $g(\alpha)$.

Isoconversional methods are basically the model-free methods and are frequently useful for the activation energy estimation without considering the reaction model. The major shortcoming of that particular model is basically the reaction mechanism evaluation, and this is necessary for pre-exponential factor estimation.

3.4 Model-free kinetics

3.4.1 Friedman method

Friedman [47] had suggested the logarithmic form of the equation.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[A\, f(\alpha)] - \frac{E_a}{RT} \quad (7)$$

By drawing the slope of ln(dα/dt) vs I/T plot at constant α the activation energy (E_a) is calculated.

The Friedman method is sensitive to noise from the experimental data because it is basically the differential isoconversional method. This noise leads in some way to errors in the estimation of E_a that is the function of conversion α. Compared to the differential methods, conversional integral methods somehow less sensitive and because of that less errors are present. Ozawa- Flynn- Wall (OFW)[48] and also Kissinger-Akahira-Sunose(KAS) are integral methods that are used.

3.4.2 Flynn-Wall-Ozawa method (FWO)

To compute thermokinetics parameters, the FWO method is the accepted method[20]. The FWO method that is derived from the approximation of Doyle's for the integral temperature. The final equation derived for FWO is represented as;

$$\ln\beta = \ln\left[\frac{A\, E_a}{R\, g(\alpha)}\right] - 5.331 - 1.052\,\frac{E_a}{RT} \quad (8)$$

From the plot of ln ß vs 1/T E_a is calculated, and the slope in this equation is -1.052E_a/R. The pre-exponential factor (A) is to be estimated using ASTM E-1641-18 by considering first-order reaction kinetics.

3.4.3 Kissinger-Akahira-Sunose (KAS) method

To calculate kinetics, another method is KAS which is to be used in iso conversion method to calculate kinetics [49]which is stated as follows.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{A\,R}{E_a\,g(\alpha)}\right] - \frac{E_a}{RT} \tag{9}$$

From the slope of ln(ß/T^2) vs I/T the activation energy of the KAS is calculated. The slope is -E_a/R.

Calculations of thermodynamic parameters

By using the equations given below different thermodynamic parameters are calculated [46].

$$\Delta H = E_a - RT \tag{10}$$

$$\Delta G = E_a - RT_p \ln\left(\frac{K_B\,T_p}{h\,A}\right) \tag{11}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_p} \tag{12}$$

Where the Boltzmann constant is 1.381×10^{-23} J/K , where h is the Planck's constant having value is 6.626×10^{-34}J. s, T_p is the peak temperature.

3.5 Model-fitting kinetics

The DAEM is the widely used model for the active solid materials thermal kinetic analysis, including coal [50-52], charcoal [53], oil shale[54, 55], polymer[56, 57], solid waste[58, 59],sewage sludge[60, 61] and biomass [62-65]. The reaction kinetics of the materials under the influence of heat can also be described by the DAEM, by which the kinetic parameters are specified, and the reaction mechanism might be postulated.

Biomass consists of many components and, during the decomposition process, each of these carries unique kinetic parameters. During combustion, the degradation rate of the particular pseudo-component [66]can be examined with respect to the conversion of any component i at any time t.

$$\frac{d\alpha_i}{dt} = A_i \exp\left(\frac{-E_{ai}}{RT}\right) f(\alpha_i) \tag{13}$$

Any time-dependent decay coefficients can be well described by the average E_a at any sort of heating rate for the non-isothermal systems, as the DAEM is valid for any of the measured time-temperature history.

$$\frac{d\alpha_i}{f(\alpha_i)} = \frac{A_i}{\beta} \exp\left(\frac{-E_{ai}}{RT}\right) dT \tag{14}$$

For the degradation of the first order pseudo-component $f(\alpha_i) = 1 - \alpha_i$

$$\alpha_i = 1 - \exp\left[-\frac{A_i}{\beta}\int_0^T \exp\left(\frac{-E_{ai}}{RT}\right) dT\right] \tag{15}$$

The non-isothermal decay of the complex material, such as the biomass, during the thermogravimetric analysis makes a good relation to the experimental data at low heating rates. A continuous distribution of the reactants for different complicated sets of reactions can be described by an integral.

$$\alpha = \int_0^\infty \left\{1 - \exp\left[-\frac{A_i}{\beta}\int_0^T \exp\left(\frac{-E_{ai}}{RT}\right) dT\right]\right\} f(E_a) dE_a \tag{16}$$

In the equation given above the density function of the activation energy is $f(E_a)$ and $f(E_a).dE_a$ is the probability density fraction which is being linked with activation energy range. This particular equation contains the double layer of integrals and is therefore harder to compute. $f(E_a).dE_a$ is normalized and sum of squared error is used to compute the kinetic parameters assuming multiple area normalized Gaussians distributions.

3.6 Methodology for Artificial neural network(ANN)

3.6.1 Artificial neural network (ANN)

An Artificial neural networks (ANN) is basically the useful tool for non-linear regression [67]. The major advantage of the ANN is that any data set can be trained without any certain knowledge of this modelled phenomenon. ANN models were being developed in that study to depict the E_a. For the non-linear regression Multilayer perceptron (MLPs) are basically used. MLP comprises different layers such as input layer, hidden layer and also the output layers. The outer layer and the hidden layer are basically made up of artificial neurons. The model input layers can transfer the signals input with the hidden layer to any output layer. During data set training, any error between the output signals and the target is minimized by careful adjustment of the neurons in the hidden layer and the transfer function of neurons. ANN uses the input and target data to build a suitable pattern in the layers. Tibco Statistica 13.5 was basically used to made the structural network using MLP regression model for the target values. In the input layer, temperature (K), conversion (-) and the heating rate (°C/min), were used as input neurons, while for the output neuron in the outer layer activation energy was used. From the original data set, three subsets were obtained, including training (70%), testing (15%), validation (15%)[68]. For the development of the ANN-based MLP regression model, Broyden-Fletcher-Goldfarb-Shanno (BFGS) was used[69]. Different built-in activation functions were used by the hidden and the output layers, which include exponential, logistic, SoftMax, hyperbolic, Gaussian and the Sin function. Neuron is basically connected to the nodes and to all the nodes with the other layers with some of the network parameters such as weights and biases. The neural network is somehow trained by the learning by reducing the sum of squared error. Automated Network Search (ANS) which is the feature of SANN has made the comparison of various networks and selected the best model on the basis of comparison that surely saves time via neglecting the lengthy time and error-based process. The ANN modelling is presented in Fig. 7 shown in as,

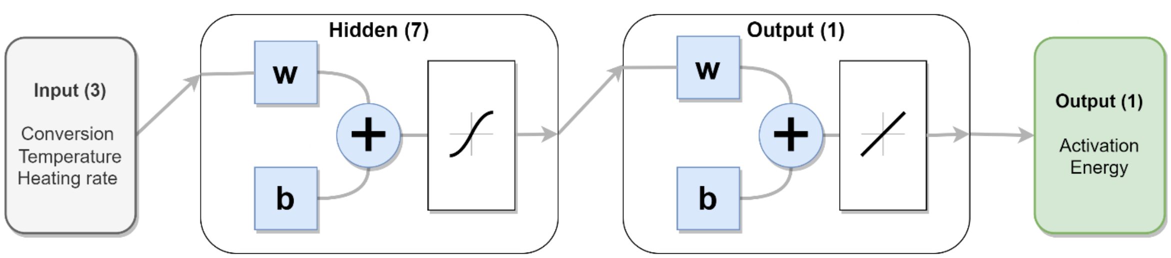


Fig.7: ANN selected network topology

Chapter 4

Results and discussion

4.1 Results and discussion

4.1.1. Physiochemical properties and characterization of sludge

Tannery sewage sludge physicochemical properties were evaluated by various techniques which include EDX, SEM, and FTIR. The results of the critical physicochemical properties are summarized in **Fig.8**. SEM is used to describe the morphology of the sludge, and EDX is used to describe elements in a specific area of the tannery sewage sludge.

The FTIR spectrum of the sewage sludge from the tannery are presented in the subsequent Fig. *8*. It can be observed from the figure that in this region various absorption bands are from 4000 to 3000 cm^{-1}. There is a region between 3400 cm^{-1} and 3000 cm^{-1} that is certainly leads to the O-H stretching vibration in alcohols and acids. Basically, in the FTIR spectra of the first region 3399 cm-1, absorption band is present which is related to N-H bond stretching of the organic compound[70]. The various compounds also present the characteristic band in 1653 cm-1, which is certainly related to the vibration of C—O of the primary amides. Although at 2923 cm^{-1} there is a small spike that leads to the C-H bonds for the cis-alkanes[70].

In fact, the other absorption band is in between 3000 cm^{-1} to 2800 cm-1, which is the indication of the presence of a hydrocarbon chain that appears on the organic material of that tannery sludge sample detected by the thermal degradation analysis. The 2923 cm^{-1} bands in 2923 cm^{-1} that led to asymmetric stretching of the C-H bonds of the methylene and methyl group. The band in 2853 cm^{-1} is relates to the symmetric stretching of the C-H bond of the methyl group. Band in 2520 cm^{-1} adheres to carboxylic acid, while the band in 1455 cm^{-1} is surely meant to the CH_2 rocking. The area between 1170 cm^{-1} and 1000 cm^{-1}, the intense band is present at 1029 cm-1, which is likely to be OH vibration of particular mineral compounds that are present in sewage sludge from the tannery, but in this region, the hydrocarbons and all the silicate compounds would absorb[71]. The band of 713 cm^{-1} and 873 cm^{-1} is basically CH_2 scissoring deformation. The 471 cm^{-1} spectrum is for the presence of alkyl halides.

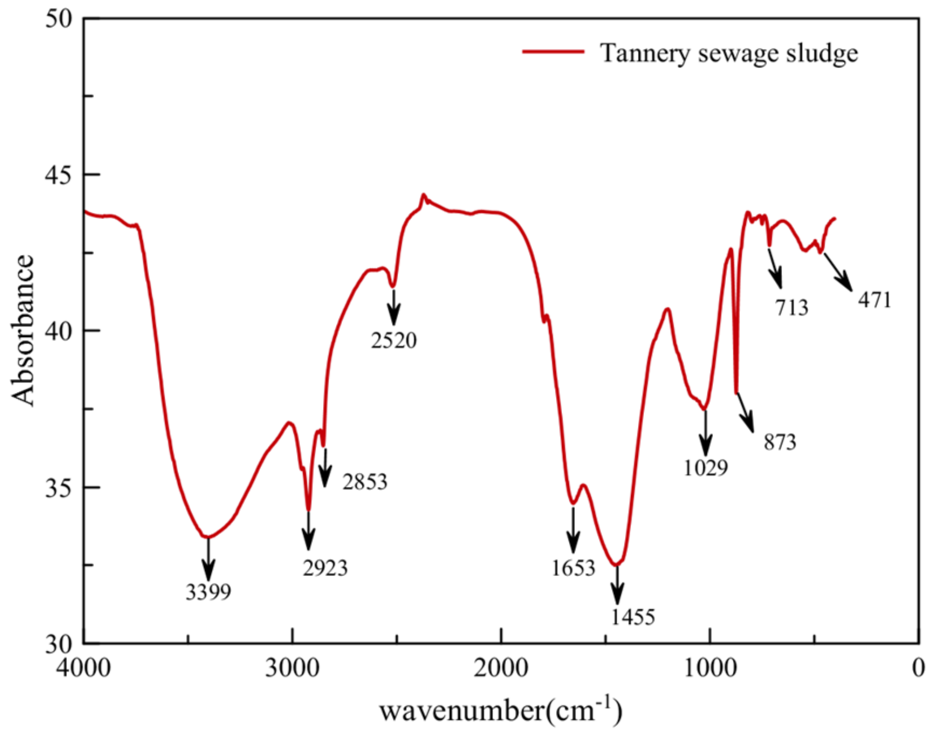


Fig. 8:FTIR spectrum of tannery sewage sludge

4.2 Thermal behavior of tannery sewage sludge combustion

Thermal behavior was being carried out at the four different heating rates (5, 10, 20, 40 °C/min) in the air atmosphere. The TG and DTG plot for combustion is presented in **Fig. 9**.

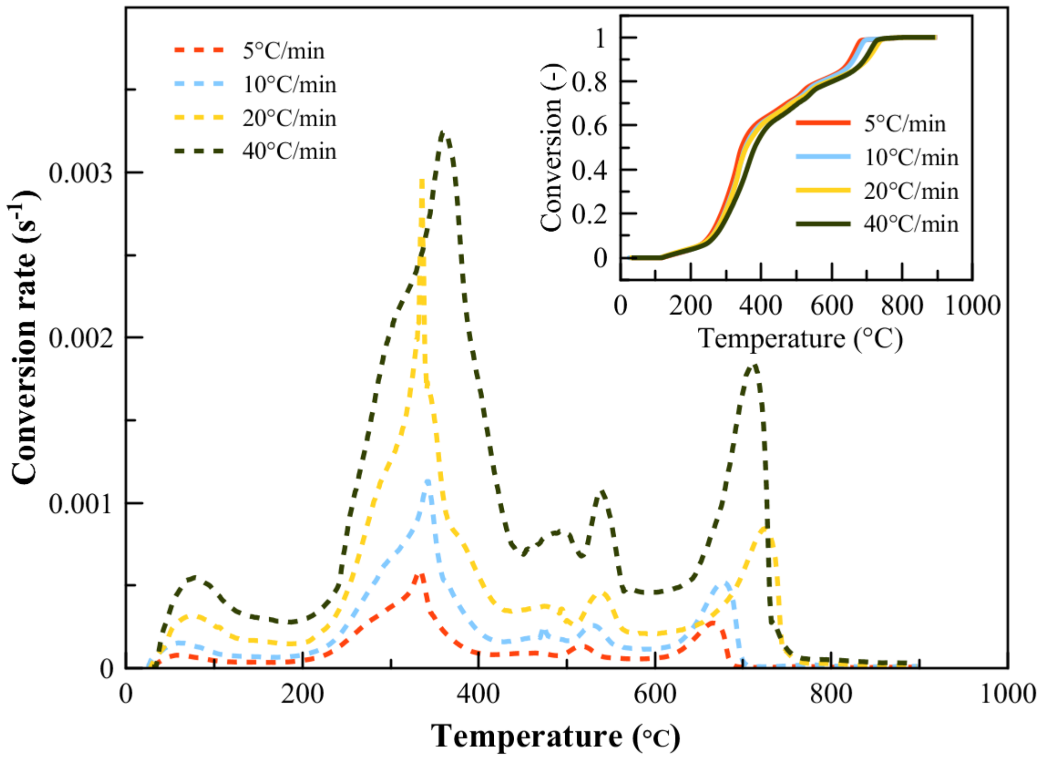


Fig.9: DTG curve of combustion at different heating rates (5 °C/min, 10 °C/min, 20 °C/min, 40°C/min)

Thermal degradation in the air atmosphere can be predicted in three stages. At the heating rates of 5, 10, 20 and 40 °C/min for the air environment, dehydration or inbound moisture will be removed in stage 1 where the temperature range is (30- 200°C). Th final temperatures at the all the heating rates would be 184.59 °C, 189.75°C, 191.65°C, and 196.73 °C. In the second phase, carbohydrates, proteins, and lipids begin to degrade. The degradation range during the combustion of stage 2 is in the range of 200°C to 600°C. Basically, the two main peaks are identified, one peat at the 300 °C and the second spike is at the 372 °C. The major combustion reaction would take place at this stage. There is an increase in peak at about 470°C and 550°C, showing that the protein and carbohydrates of the sample will degrade for all heating rates. However, interestingly, there is a sharp curve at the temperature of 550 ° C that shows the maximum degradation of lipids at this point. In the third stage, all the carbonaceous material and the lignin part of the sample will start to degrade during the combustion reaction. Lignin is basically amorphous with a cross-linking structure with no exact structure and its degradation range for the sludge is 600 ° C to 800 ° C. In this particular case, analysis is basically difficult because of the formation of complex species during the degradation of lignin. Also, the other carbonaceous material will start to degrade as the heat propagate breakage of the bonds occurs, and because of this, maximum mass loss will occur. For the heating rate of 5 °C/min and the 10 °C/min the peak appears at 670 °C while it is 710 °C and 730°C at 40 °C/min and the 20 °C/min. It can be interestingly seen that the lignin degradation temperature is the same for the heating rates of 5 °C, 10 °C/min and it is different from the other heating rates, which are 20 °C/min and 40 °C/min. Therefore, as the heating rate increased, the peak temperature also increased. It is interesting that degradation studies of the lignin separation will not surely match the thermal behavior of the components. Initial and final temperatures and weight loss of all three stages are presented in Table 2

Table 2: Initial. Final temperature and weight loss of tannery sewage sludge at different heating rates

Heating Rate (˚C/min)	**T_i (˚C)**	**T_f (˚C)**	**Mass loss (%)**
Stage 1			
5	30	184.59	4.36
10	30	189.75	4.586
20	30	191.65	4.794
40	30	196.73	4.4
Stage 2			
5	184.59	553.16	37.104
10	189.75	558.5	37.374

20	191.65	586.11	36.606
40	196.73	596	37.3
Stage 3			
5	553.16	800	10.218
10	558.5	800	10.36
20	586.11	800	9.782
40	596	800	10.28

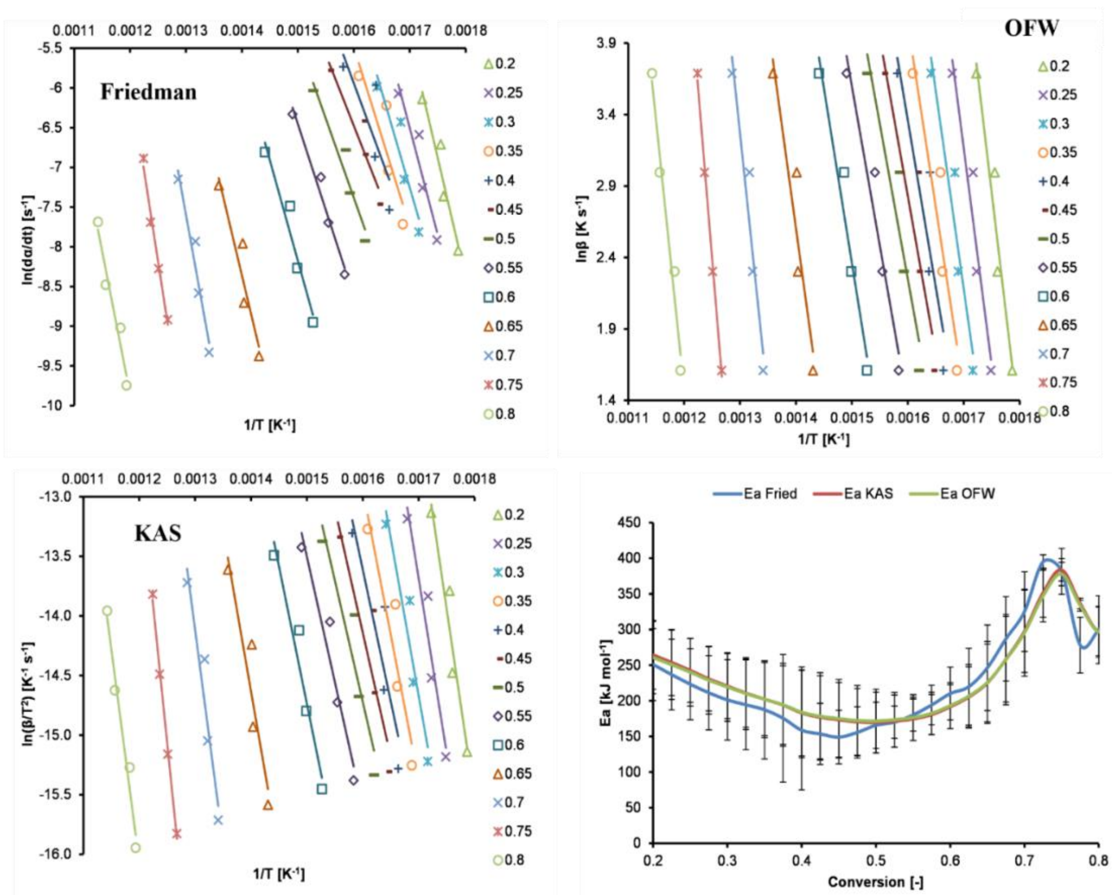


Fig.10: Typical linear fit plot of the Friedman, KAS and OFW isoconversional model and variation in apparent activation energy

4.3 Thermal behaviour of tannery sewage sludge pyrolysis

The resulting TG and the DTG plots for the tannery sewage sludge in the nitrogen environment are given in Fig. 11. This figure would indicate that tannery sewage sludge thermal decomposition is being classified into three different stages: stage 1 (Dehydration), stage 2 (proteins, carbohydrates, and lipids degradation) stage 3 (decomposition of lignin). The mass loss during the pyrolysis of Tannery Sewage sludge (TSW) in the stage 1 is generally due to the loss of inbound moisture content and it is estimated between the range of temperature of 30°C to 200°C for all the determined heating rates. In the stage 2 it was observed that organic constituents which include lipids, proteins and the carbohydrates will degrade. The two peaks are identified in the DTG plot: one at the temperature of 305°C and the other temperature is 340°C that represents that the protein, and the carbohydrates are being degraded. There is a rise in peak at the 470°C and 550°C which represents the degradation of the lipids. In the 3rd stage carbonaceous material and the lignin will start to degrade and the weight loss of the sample will occur. There is a peak at about the 760°C which represents the maximum mass loss of the sample. With the changing heating rates the total weight loss is not noticeable during the pyrolysis. The mass loses are very close to each other at every stage of the same heating rate. With the increasing heating rate, the peak temperatures are increased. As in the stage 2, they were 305°C and 470°C at the heating rate of 5°C/min and it became 340°C and 480°C at the heating rate of 20°C/min respectively. In the stage 2 the peak temperature depicts that main pyrolysis reactions occurred at this stage. Hence it shows that at the lower heating rates lower temperature required.

Therefore, the energy demand for the pyrolysis process would increase as the heating rate increases. Addition to that with the increase of heating rates shifting the boundaries of the higher temperature stages as well as the peak temperatures. Exactly the similar kind of effect are reported in the studies for the sludge and the sludge compost at the higher heating rates.

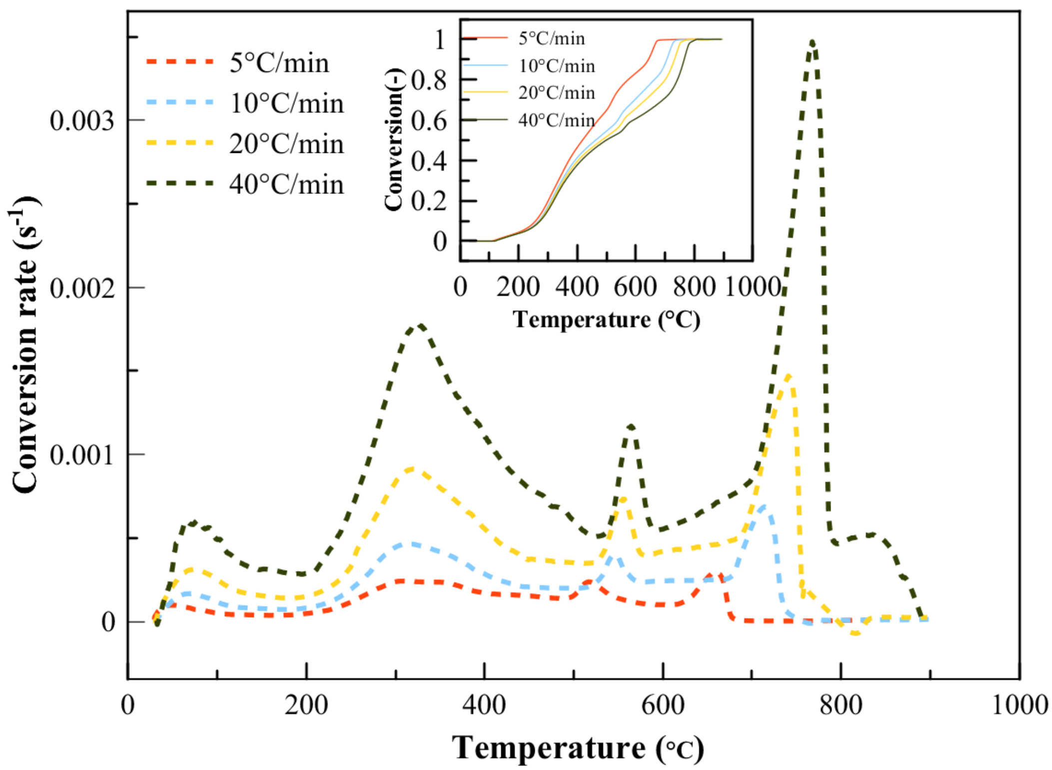


Fig.11: DTG curve of pyrolysis at different heating rates (5 °C/min, 10 °C/min, 20 °C/min, 40°C/min)

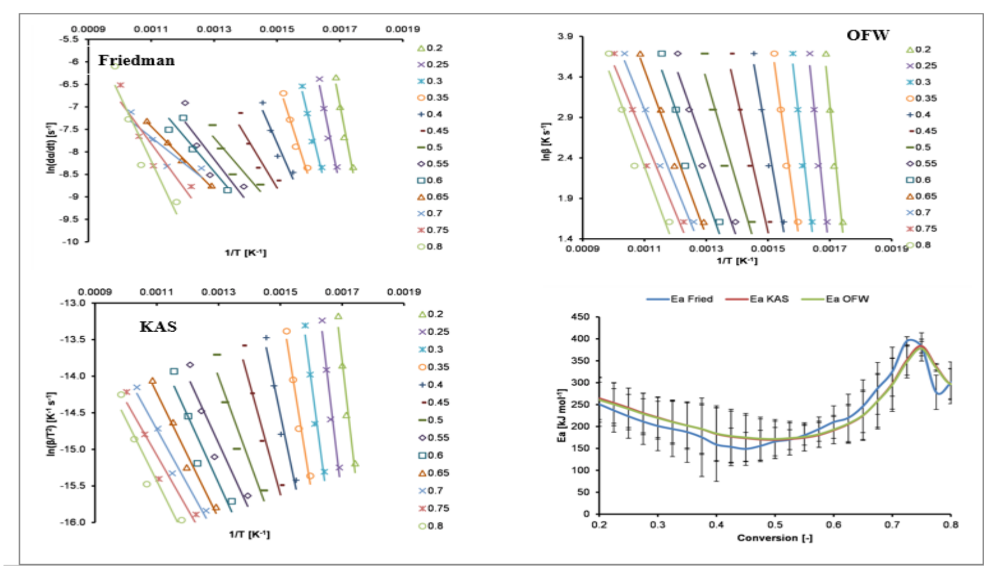


Fig. 12: Typical linear regression plot of pyrolysis and its apparent activation energy

4.4 Kinetic and thermodynamic analyses of combustion

The ease with which the sludge would disintegrate can be represented by the kinetic parameter of the activation energy. By linear fitting in the non-isothermal data using the model-free method the different values of activation energy are calculated. The different models include the Friedman method, KAS, and the OFW method at the four heating rates in the air atmosphere. By the corresponding slopes of the different models, E_a can be calculated from the conversion degree from 0.1 to 0.8 with the help of the distribution coefficient (R^2). In the Table 3 all the values of activation energy and pre-exponential factor are presented. It can be seen that for the Friedman E_a decreases as the conversion increases to 0.475. E_a at this point would be 155.64kJ/mol. As the conversion increases from 0.5 to 0.725, an increase in E_a is observed, which is 165.68kJ/mol to 395.23kJ/mol. Also, the linear regression decreases from 0.925 to 0.904 as we move from conversion 0.2 to 0.45. The maximum linear regression is observed at the conversion of 0.725 which is 0.999 at which the Ea is 395.23kJ/mol. KAS and OFW are the relative and approximate solutions to calculate Ea. Linear fitting fits well for all isoconversional methods. R^2 for KAS and OFW is 0.999 at a conversion of 0.75. Due to the sharp weight loss at stage 2, the average activation energy(Ea) for Friedman, KAS, OFW are 226.04 kJ/mol, 230.71 kJ/mol, and 230.11 kJ/mol, respectively.

Different thermodynamic parameters which include Gibbs free energy enthalpy and entropy, were being calculated in the air environment. System total energy for activated complex development is certainly represented by Gibbs free energy[72]. All of the enthalpy values are positive at every conversion, which certainly meant that the nature of the reaction is endothermic. At conversion from 0.2 to 0.8 the Gibbs free energy values decrease, which depict the system energy for the activated complex. The change in entropy is negative at the conversion degree of 0.425 to 0.6, which indicates that the substances produced are very well organized in molecular structure in this particular region[73].

Table 3: Activation energy (E_a) and thermodynamic parameter calculated by the Friedman, KAS, and OFW method in combustion.

	Friedman Method		**KAS Method**		**OFW Method**					
α	**E_a, kJ mol^{-1}**	**R^2**	**E_a, kJ mol^{-1}**	**R^2**	**E_a, kJ mol^{-1}**	**R^2**	**A, s^{-1}**	**ΔH, kJ mol^{-1}**	**ΔG, kJ mol^{-1}**	**ΔS, J mol^{-1} K**
0.200	250.79	0.925	264.47	0.931	260.64	0.936	5.90E+21	257.32	159.61	160.49
0.225	236.79	0.919	253.86	0.931	250.66	0.936	4.19E+20	247.33	163.02	138.47
0.250	223.32	0.909	242.73	0.929	240.18	0.934	2.92E+19	236.83	166.03	116.28
0.275	211.27	0.891	230.74	0.922	228.85	0.928	1.85E+18	225.49	168.68	93.31
0.300	201.32	0.864	220.72	0.913	219.42	0.920	1.86E+17	216.04	170.85	74.22
0.325	194.41	0.826	210.85	0.897	210.12	0.905	2.08E+16	206.73	172.64	55.98
0.350	187.44	0.786	202.33	0.876	202.10	0.886	3.22E+15	198.68	174.08	40.42
0.375	175.53	0.657	194.08	0.848	194.32	0.861	5.54E+14	190.89	175.21	25.76
0.400	158.78	0.642	183.03	0.806	183.88	0.823	5.97E+13	180.44	176.05	7.21

0.425	153.57	0.865	176.93	0.806	178.15	0.824	1.59E+13	174.69	177.01	-3.82
0.450	148.96	0.886	173.46	0.832	174.92	0.848	6.73E+12	171.44	178.14	-10.99
0.475	155.64	0.904	170.48	0.857	172.16	0.871	3.09E+12	168.67	179.32	-17.49
0.500	165.68	0.929	169.65	0.878	171.47	0.891	2.03E+12	167.96	180.75	-21
0.525	170.06	0.965	171.54	0.908	173.39	0.918	2.00E+12	169.86	182.74	-21.15
0.550	180.14	0.970	174.60	0.937	176.44	0.944	2.27E+12	172.89	185.15	-20.13
0.575	194.08	0.961	180.62	0.949	182.34	0.954	4.15E+12	178.78	188.0	-15.15
0.600	210.06	0.941	191.61	0.945	193.05	0.951	1.60E+13	189.47	191.86	-3.93
0.625	219.76	0.892	205.30	0.914	206.47	0.923	7.49E+13	202.88	197.48	8.86
0.650	246.29	0.893	225.15	0.885	225.75	0.895	6.58E+14	222.14	205.77	26.89
0.675	287.02	0.922	258.36	0.893	257.67	0.902	4.12E+16	254.04	216.74	61.27
0.700	325.28	0.944	297.62	0.923	295.39	0.929	5.39E+18	291.75	229.80	101.75

0.725	395.23	0.999	351.66	0.979	347.16	0.981	3.40E+21	343.50	248.93	155.33
0.750	381.76	0.986	383.75	0.996	377.85	0.997	8.50E+22	374.17	263.33	182.05
0.775	278.16	0.962	336.66	0.999	333.62	0.999	3.26E+19	329.92	258.90	116.64
0.800	299.79	0.952	297.48	0.972	296.83	0.974	2.28E+16	293.11	253.90	56.20
Average	**226.04**		**230.71**		**230.11**		**3.79 E+21**	**226.60**	**194.76**	**52.30**

4.5 Kinetic and thermodynamic analysis of pyrolysis

Activation energy is basically the critical kinetic parameters that surely gives an idea that how easily the sludge would disintegrate. Ea predicts that the minimum quantity of energy required for the breakage of the chemical bond and surely it is also responsible for the sensitivity and the reactivity of a reaction rate. Ea was being calculated by the linear fitting in the non-isothermal TG data using the model free isoconversional method which include Friedman, KAS and the OFW at the four heating rates. From the corresponding slopes of each of the line the activation energies (E_a) can be calculated from the conversion degrees (α) from 0.1 to 0.8 with the corresponding linear regression (R^2). All values of the activation energies, pre-exponential factor decreases with the increase of the conversion degree to about ((α=0.7) and then activation energy starts increasing with (α= 0.725 to (α=0.8). By all three iso conversional methods the linear fitting fits well with the correlation coefficient (R^2) which is 0.994 at α=0.65 for Friedman method. The isoconversional model free plots fits well for the relation because it is the main solution.

The reason for this is that due to sharp weigh loss at the temperature range of 200°C to 400C. the average activation energies calculated by Friedman, KAS, OFW was found to be 130.9 kJ $mol^{-1,}$ 143.14 kJ mol^{-1}, 147.91 kJ mol^{-1} respectively.

Enthalpy change, Gibbs free energy and the Entropy as the thermodynamic parameters were determined for the TSS pyrolysis at all the conversion values. The enthalpy values were positive for changing conversion degree that means that during the pyrolysis the reactions were endothermic. Gibbs free energy represents the total energy increase in the system for the activated complex development. The Gibbs free energy are in the range of 165.38 and 211.87 for all the models. The entropy changes for less than α= 0.3 are positive and greater than that the entropy changes are negative. The negative values of delta s indicate that produced substances are well organized in the molecular structure as compared to the initial substance that shows that before reaching at the thermodynamic equilibrium the substances undergo the chemically and the physically ageing process.

Table 4: Activation energy (E_a) and thermodynamic parameter calculated by the Friedman, KAS, and OFW method for pyrolysis.

	Friedman method		**KAS method**		**OFW method**					
α	**E_a, kJ mol^{-1}**	**R^2**	**E_a, kJ mol^{-1}**	**R^2**	**E_a, kJ mol^{-1}**	**R^2**	**A, s^{-1}**	**ΔH, kJ mol^{-1}**	**ΔG, kJ mol^{-1}**	**ΔS, J mol^{-1} K**
0.200	300.91	0.957	303.20	0.955	297.69	0.957	#DIV/0!	294.33	--	--
0.225	296.42	0.956	300.36	0.956	295.12	0.959	5.73E+23	291.76	211.12	199.05
0.250	286.65	0.957	294.82	0.957	290.00	0.960	9.02E+22	286.62	211.87	183.63
0.275	266.69	0.959	283.44	0.960	279.33	0.962	4.74E+21	275.93	210.84	159.10
0.300	238.91	0.962	264.44	0.964	261.42	0.966	6.25E+19	258.00	207.40	123.07
0.325	209.58	0.961	240.88	0.968	239.18	0.970	3.90E+17	235.75	202.36	80.82
0.350	180.15	0.951	215.26	0.969	214.97	0.972	1.87E+15	211.52	196.42	36.36
0.375	154.60	0.935	190.53	0.966	191.63	0.969	1.17E+13	188.16	190.59	-5.83
0.400	131.03	0.911	166.65	0.959	169.11	0.963	9.43E+10	165.62	184.90	-45.97

0.425	112.55	0.884	145.00	0.950	148.73	0.957	1.22E+09	145.23	179.86	-82.18
0.450	95.83	0.842	125.99	0.937	130.89	0.946	2.70E+07	127.37	175.62	-113.89
0.475	80.58	0.805	109.33	0.916	115.30	0.930	9.82E+05	111.76	172.01	-141.48
0.500	67.27	0.814	95.44	0.905	102.38	0.922	6.48E+04	98.82	169.06	-164.13
0.525	53.90	0.855	82.73	0.917	90.62	0.935	5.89E+03	87.04	166.25	-184.10
0.550	74.45	0.761	75.84	0.904	84.30	0.927	1.45E+03	80.70	165.38	-195.81
0.575	86.80	0.818	75.86	0.866	84.53	0.897	1.20E+03	80.91	166.73	-197.43
0.600	68.10	0.851	76.42	0.894	85.39	0.919	1.20E+03	81.75	168.05	-197.48
0.625	61.69	0.953	74.25	0.948	83.67	0.961	7.69E+02	80.01	168.40	-201.21
0.650	58.57	0.994	71.24	0.971	81.11	0.979	4.05E+02	77.44	168.65	-206.57
0.675	47.15	0.823	67.24	0.968	77.56	0.977	1.93E+02	73.87	168.33	-212.79
0.700	46.05	0.789	63.24	0.958	73.96	0.970	9.48E+01	70.25	167.87	-218.73
0.725	57.85	0.826	60.92	0.946	71.94	0.962	6.04E+01	68.21	168.04	-222.52
0.750	78.82	0.851	61.32	0.931	72.49	0.952	5.67E+01	68.75	169.35	-223.09
0.775	96.80	0.853	64.23	0.914	75.46	0.940	7.51E+01	71.69	171.79	-220.81
0.800	121.19	0.886	69.85	0.901	81.01	0.929	1.45E+02	77.22	175.36	-215.37
Average	**130.90**		**143.14**		**147.91**		**--**	**144.35**		

4.6 Distributed activation energy model (DAEM)

Fig. 13 shows the distribution of activation energies for the combustion of sewage sludge from the tannery.

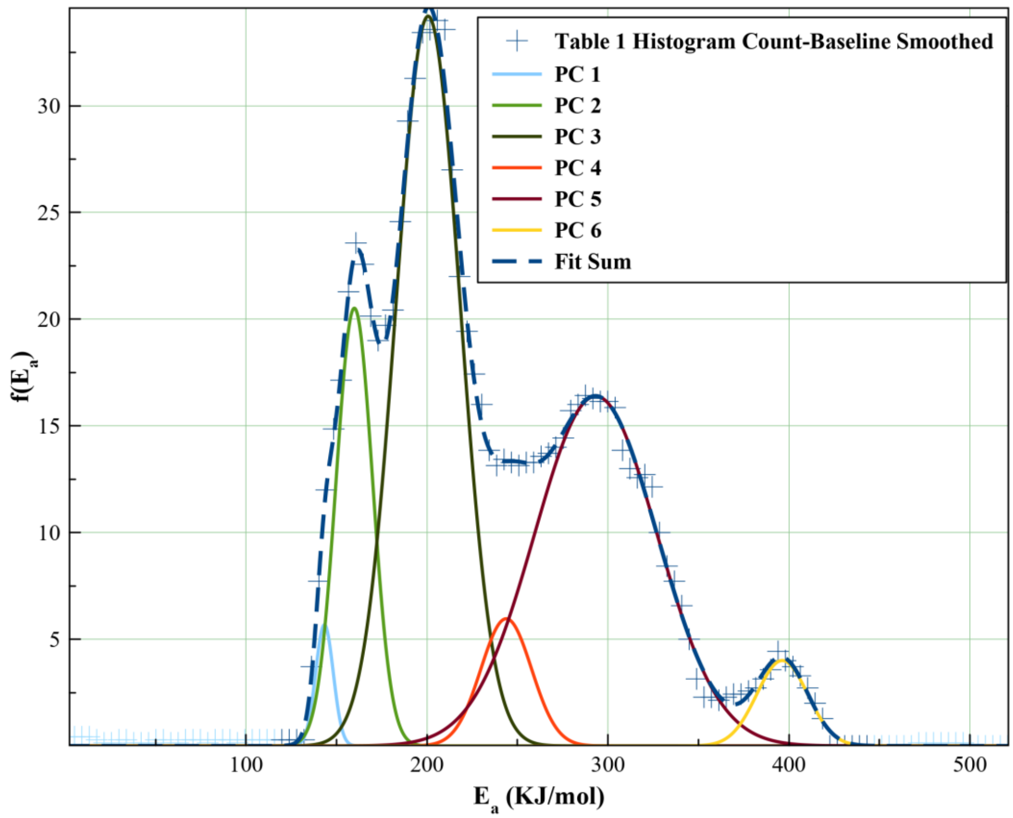


Fig.13:Distribution function of six pseudo-components of combustion

The activation energies distribution could be visualized as the convolution of six probability distribution functions named as the pseudo-components (PC1, PC2, PC3, PC4, PC5, and PC6). The PC3 has a sharp peak and a large amplitude with an Ea of 200.62 kJ/mol. However, the PC2 Ea is lower than PC3. PC5 has the broader peak with higher E_a than PC2 and PC3. The E_a of PC4 is in the range of PC3 and PC5. PC6 has the highest activation energy among all of them. Although PC1 has the sharp peak and low amplitude, it has the lowest Ea among all of them, which is about 69.48kJ/mol.

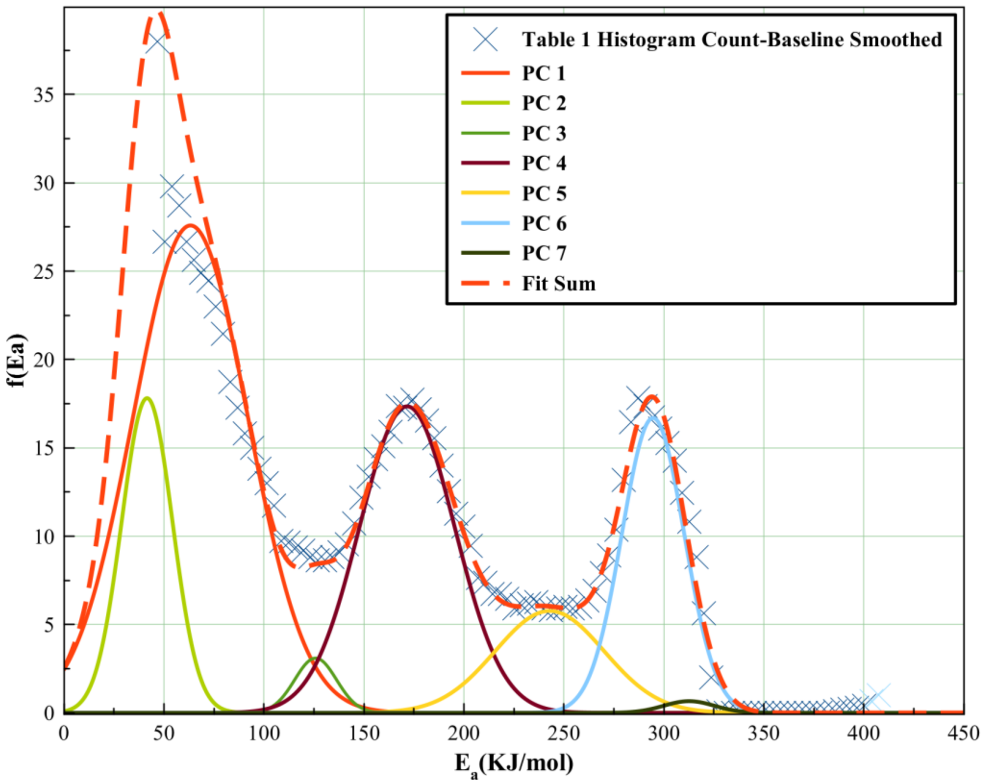


Fig.14: Distribution Function of seven pseudo-components for pyrolysis

The distribution of activation energies of the tannery sewage sludge in the nitrogen environment are presented in the Fig.14. The distribution of activation energy is visualized by the seven-probability function to be named as the pseudo components as PC1, PC2, PC3, PC4, PC5, PC6, PC7. PC1 has the large amplitude among all and has the Ea of 63.25KJ/mol. PC 7 has the lowest peak and smaller amplitude among all of the components where its Ea is higher among all (312.61KJ/mol). While lowest Ea among all the components is for PC2 which is 41.5KJ/mol. The other components ,PC3,PC4,PC5,PC6 has the intermediate Ea. The all parameters of the DAEM for the air and the nitrogen are given in the Table 5.

Table 5:Kinetic parameters of the combustion and pyrolysis of tannery sewage sludge obtained from DAEM

Pseudo-component for combustion	**Pseudo-component for pyrolysis**	**Parameters***	**Tannery sewage sludge combustion**	**Tannery Sewage sludge pyrolysis**
PC1	PC1	Area	69.48	1988.9362
		Ea (kJ/mol)	143.31	63.2561
		HWHM	5.75	33.86
PC2	PC2	Area	519.20	568.79
		Ea (kJ/mol)	159.85	41.54
		HWHM	11.89	15
PC3	PC3	Area	1519.45	81.05
		Ea (kJ/mol)	200.62	125.83
		HWHM	20.87	12.2995
PC4	PC4	Area	208.84	1035.024
		Ea (kJ/mol)	243.77	171.5871
		HWHM	16.46	28.0242
PC5	PC5	Area	1389.27	17.3482
		Ea (kJ/mol)	293.27	393.6048
		HWHM	39.81	242.8832
PC6	PC6	Area	141.02	32.0457
		Ea (kJ/mol)	396.29	653.3329
		HWHM	16.55	294.6114

	PC7	Area		18.3891
		Ea (kJ/mol)		21.0998
		HWHM		312.6113
				15

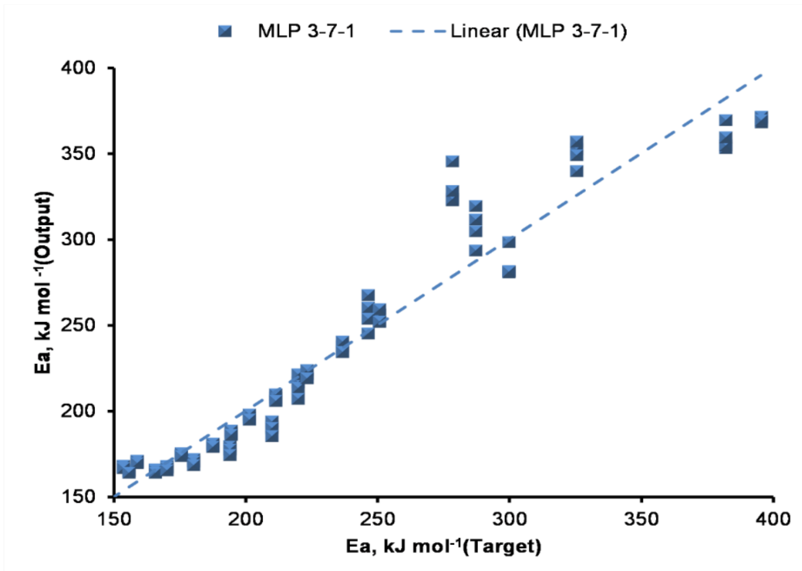
* HWHM is half width at half maximum

4.7 Prediction using an artificial neural network

The ANN regression model based on MLP was trained, and a better model was retained. Based on the sum of squared errors which is the lowest and the highest correlation coefficient during the validation, training, and testing of the data sets. For different heating rates, the structure of the best performing networks was MLP-3-7-1 for the air environment. ANN modeling based on MLP consisted of seven hidden layers for the combustion environment with their Tanh functions in the middle layers, and the exponential functions for the output layers that somehow returned the excellent correlation coefficient. MLP-3-7-1 for combustion is being used to understand the conversion of tannery sewage sludge.

The regression graph in the following figure shows the target and model output values. For good agreement, there must be a high correlation coefficient of the model with the output values and experimental target values. Fig. 15(a) shows the regression plot the output of the ANN model based on the target values.

(a)



(b)

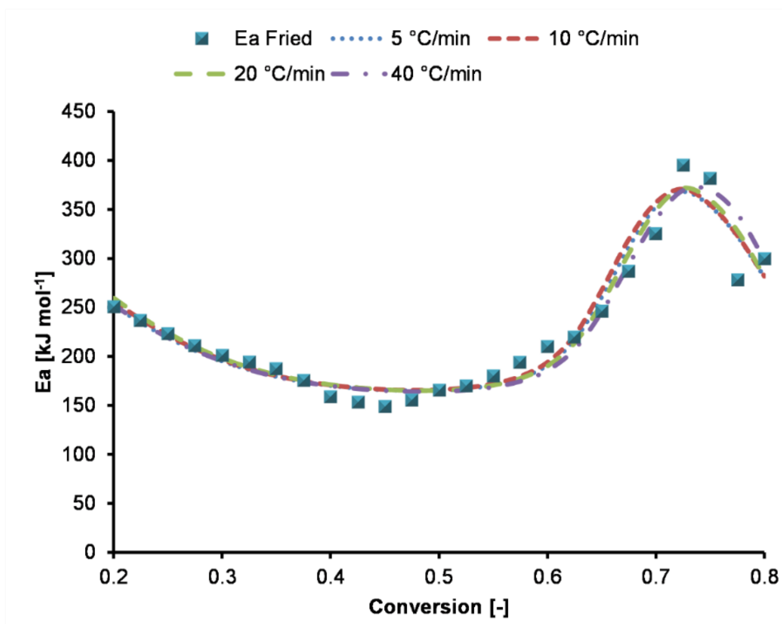
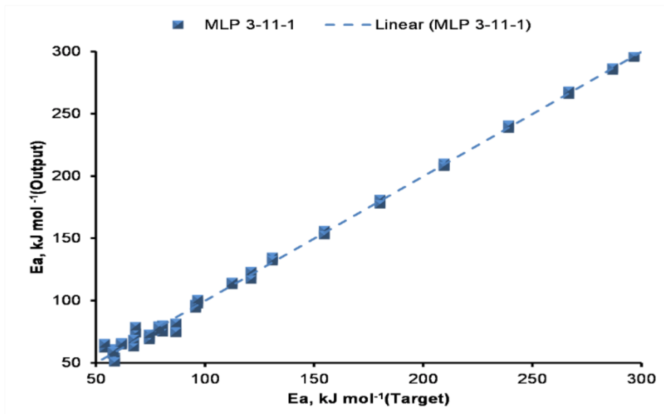


Fig. 15 Correlation between (a) output and target for different input parameters with best-fit MLP and (b) E_a and conversion with experimental and the predicted values

The regression graph in the following figure shows the target and model output values for the pyrolysis. For good agreement, there must be a high correlation coefficient of the model output with the experimental target values. Fig.16 shows the best fit model for pyrolysis between the experimental and the target values.

(c)



(d)

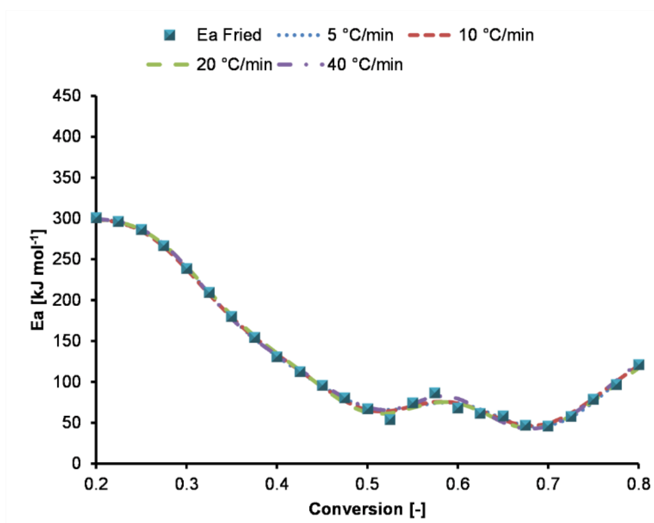


Fig.16 Correlation between (c) output and target for different input parameters with best-fit MLP and (d) E_a and conversion with experimental and the predicted values

The model summary for training, validation, and the testing is described in Table 6

Table 6: Summary of networks (training, testing, and validation) for combustion

Net. name	**Training perf.**	**Test perf.**	**Validation perf.**	**Training error**	**Test error**	**Validation error**	**Training algorithm**	**Error function**	**Hidden activation**	**Output activation**
MLP 3-7-1	0.973565	0.987263	0.941037	126.4811	112.5599	248.3278	BFGS 39	SOS	Tanh	Exponential
MLP-3-11-1	0.9989	0.9986	0.9974	7.3236	15.62	11.18	BFGS 315	SOS	Logistic	

The graph is plotted between the experimental E_a values versus conversion, and the values of the MLP-3-7-1 model are plotted at the heating rates of 5°C/min, 10°C/min, 20°C/min, 40°C/min. The summary of model quality is predicted in Table 7. For -the air atmosphere, the absolute mean error from the experimental values is found to be 12.41818 while the adjusted R^2 for non-linear regression is 0.93525. for the validation of the data, the 100 data points would be taken.

Table 7:Model Quality summary of both combustion and pyrolysis

Net.name	**Mean error**	**Absolute mean error**	**Mean squared error**	**Root mean squar**	**R squared**	**Adjusted R squared**	**Sum of squar**	**Sum-squared**	**Valid N**

				ed error			**ed error**	**regress ion**	
MLP 3-7-1	- 0.883 8	12.41 818	291.3 275	17.06 832	0.935 253	0.9352 53	29132 .75	449946 .4	100
MLP 3-11-1	- 0.004 25	2.975 706	17.78 645	4.217 398	0.997 481	0.9974 81	1778. 645	706135 .8	100

The Fig. 17 predicts that three input variables which include conversion, Temperature (K) and the heating rate for the validation of result. The input conversion has more influence to predict the result for the better validation of result and its relative sensitivity is up to 75% in comparison with the other input variable which include temperature having the sensitivity of about 20% and the heating rate 5%. This shows that from all of the input variable the influence of heating rate in predicting the result is less. Similarly for the pyrolysis the influence of conversion degree is somehow has more influence than the other two input variables which include temperature and the heating rates. The relative sensitivity of conversion in the results validation is 78%. Although it is 20% for the temperature and the 2% for the heating rates.

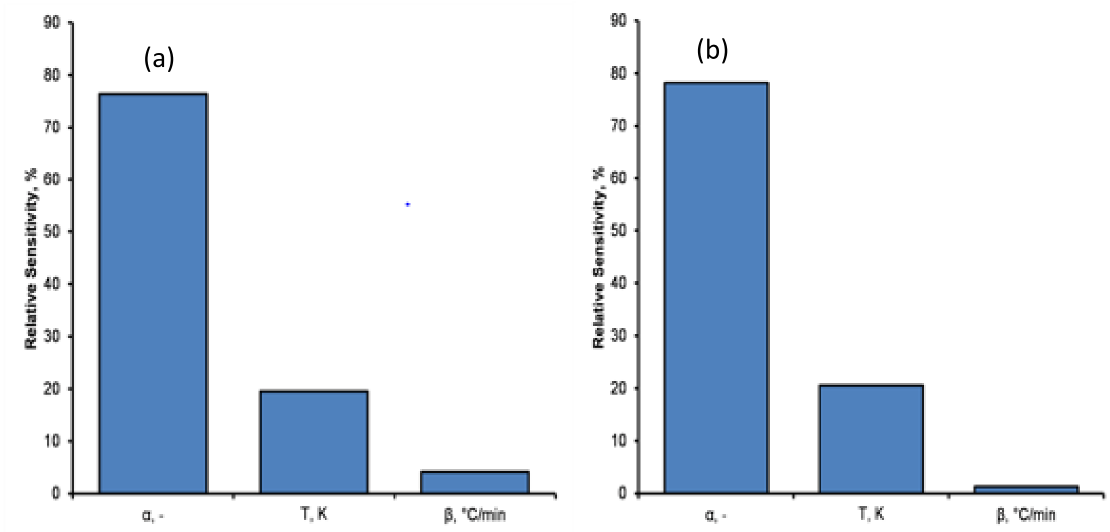


Fig.17: Influence of input variables for the model prediction in (a) combustion (b) pyrolysis

Conclusion

The combustion and pyrolysis of the tannery sewage sludge is a plausible solution to enable the industry to use the effluent that is produced uninterrupted. A key focus and development are required to evaluate and elaborate on the nature of the products being manufactured by this approach. Kinetic behavior is one way to improve the understanding of the products that are formed as a result of combustion. Depending on the mechanical and the chemical processes adopted to process the raw hide, characteristics of tannery waste can vary. During the processing stages, about 20% of the material certainly results as the solid waste which consists of scraps, proteins that are soluble The number of effluents that will be discharged are higher in volume. Care must be taken to ensure safe disposal methods to assure safety. If safe measures are not taken, then severe environmental problems can be imposed on the environment. For the preservation of hides and the skin Shaked salts are used. If it is thrown at the open dumping site in any area, then possibly groundwater pollution may occur when rain washes it away. Low ph of the tannery effluents, can surely cause the corrosion of the water carrying system. High BOD demand and the large ph, fluctuations caused by the effluents of tannery can surely kill the natural life. During the process of sulphides, the toxic gas hydrogen sulphides is produced in the highly toxic tannery effluent. During the tanning operations, chromium tanning additives are being added. Still, only some portion of these additives or agents remains in the skin hide, and a lot of fractions will remain in the tanning bath, which ultimately leads to sludge. From the chromium-containing proteins the chicken feeds are mostly produced that cause the direct entry of chromium in the food chain This study develops the knowledge on model-free kinetics in an air environment and also the thermogravimetric study of tannery sewage sludge. Also, in the present study, an artificial neural network study is employed to predict thermal degradation behavior. The major decomposition of the sewage sludge of the tannery happened in the stage 2 which is 200 °C - 600 °C where the maximum mass loss occurred. Positive values of ΔH depicts that combustion reactions are endothermic. Positive values of the ΔG and negative values from ΔS show the non-spontaneity of the process. The R^2 values also show a very good agreement for combustion. This study also investigated the frequency distribution of the activation energy by applying DAEM. The six pseudo-components are involved in the frequency distribution of the combustion environment. For a better prediction of the data, MPL-3-7-1 fits well for the experimental and the modeled values of E_a for combustion and proved to be the best model for predicting the E_a values.

Future Recommendations

- Different kinetic models should be established at multiple heating rates to investigate the best functioning condition to design process to obtain the maximum yield with lower investment.
- For the deep understanding of the kinetics and the thermodynamics model fitting approach by Coats Redfern Method to study the reaction mechanism should also be utilized.
- For the better understanding of Ea different input parameters (heating rate) to predict the Ea should also be utilized that can give the best MLPs.
- For the distribution of activation energy (DAEM) more Gaussian can also be applied to predict the pseudo components for the frequency of distributed activation energy.

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