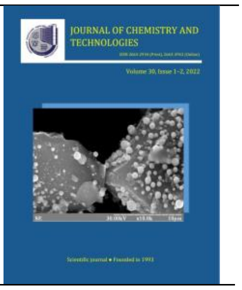
Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua



UDC 661.665.1.663.584.6

PYROLYSIS AND KINETIC STUDY OF THERMAL DEGRADATION OF WALNUT SHELLS AND INDIGENOUS COAL

Hafiz Miqdad Masood[1]*, Najaf Ali[1], M. Ashraf[2], Muhammad Shoaib[1]
[1] Department of Chemical Engineering, NFC-Institute of Engineering and Fertilizer Research, Faisalabad
[2] Research and Development Department, NFC-Institute of Engineering and Fertilizer Research, Faisalabad

Received 3 January 2022; accepted 30 March 2022; available online 28 April 2022

Abstract

Pakistani coal has a serious issue with its pre-treatment.That's why the blend of coal and walnut shells is used in present research to utilize alarge reserve of coal by means ofwalnut shells. The present study used a 50 : 50 ratio of both feedstocks, which were pyrolyzed in fixed bed reactor. The thermal degradation of the blend of walnut shells and coal was investigated by TGA and DTG analysisat different heating rate of 10, 20 and 25 °C/min. At 427 °C and 25 °C/min,the maximum degradation of blend was observed, indicatingthat 26.4 % of the bio-oil and 39% of the biochar fraction could be used for fuel. The minimum amount is preferred for the activation energy that is obtained at low conversion, and the highest amount of activation energy of 190 kJ/mol is obtained at a conversion of 0.6. The biochar obtained after pyrolysis of a mixture of walnut shells and charcoal was also characterized by proximate analysis, and elemental analysis showed that the sulfur fraction decreased from 4.48 % to 0.85 % and the heating value increased to 22.4 MJ/kg.

Keywords: Pyrolysis, Thermal degradation, Kinetic study, Flynn Wall Ozawa (FWO), Kissinger method and Thermo-gravimetric analysis (TGA)

ПІРОЛІЗ ТА КІНЕТИЧНЕ ДОСЛІДЖЕННЯ ТЕРМІЧНОГО РОЗКЛАДАННЯ ШКАРАЛУПИ ВОЛОСЬКОГО ГОРІХА ТА МІСЦЕВОГО ВУГІЛЛЯ

Хафіз Мікдад Масуд[1]*, Наджаф Алі[1], М. Ашраф[2], Мухаммад Шоаіб[1]
[1] Факультет хімічної інженерії, NFC-Інститут інженерних досліджень та добрив, Фейсалабад
[2] Відділ досліджень та розробок, NFC-Інститут інженерії та досліджень добрив, Фейсалабад

Анотація

Попередня обробка пакистанського вугілля є серйозною проблемою. Тому в цьому дослідженні використовується суміш вугілля та шкаралупи волоського горіха для збагачення великої кількості вугілля за допомогою шкаралупи волоського горіха. У цьому дослідженні використовували співвідношення обох видів сировини 50 : 50, яка піролізувалися в реакторі з нерухомим шаром. Термічне розкладання суміші шкаралупи волоського горіха і вугілля було досліджено за допомогою ТГ-ДТА аналізу при різних швидкостях нагрівання 10, 20 і 25 °C/хв. За 427 °C і 25 °C/хв спостерігалося максимальне розкладання суміші, що вказує на те, що 26.4 % біомасла та 39 % фракції біовугілля можуть бути використані як паливо. Мінімальна кількість краща для активації енергії при низькій конверсії, а найбільша кількість енергії активації 190 кДж/моль отримується при конверсії 0.6. Біовугілля, отримане після піролізу суміші шкаралупи волоського горіха та деревного вугілля, також було охарактеризовано за допомогою технічного аналізу, а елементний аналіз показав, що частка сірки знизилася з 4.48 % до 0.85 %, а теплотворна здатність збільшилася до 22.4 МДж/кг.

Ключові слова: піроліз, термічне розкладання, кінетичне дослідження, метод Флінна-Уолла-Озави (FWO), метод Кісінджера, термогравіметричний аналіз (TGA).

**Corresponding author: e-mail: miqdad_masood@outlook.com*

doi: 10.15421/jchemtech.v30i1.250520

Introduction

As a whole globe is now facing the serious issues related to energy crisis and climate change, due to the continuous decrease in fossil fuels reserves and excessive emission of greenhouse gases, respectively. For the fossil fuels an inspiring and sustainable alternative source of energy is bio-energy [1]. Biomasses are the major resource for bio-energy and it is a clean, storable and transmittable renewable energy resource. As a step towards sustainable energy, the co-processing of biomass ad coal is more preferable [2]. The environmental impact of using coal can also be minimized. Co-processing reduces CO_2 emission as well as the NO_x and SO_Xemissions can also be handled easily.

Biomass is environmental friendly source for the production of the renewable energy. As compared to the fossil fuels, biomass has less sulfur, is cheaper, and emits less carbon dioxide. The holocellulose (cellulose, hemicelluloses) are those components of biomass which are responsible for the volatile matters in pyrolysis. Biomass contains more volatile matters as compared to the coal [3]. From biomass the H and OH radicals are released during the pyrolysis which helps in the cracking of aromatic rings of coal [4, 5]. In pyrolysis at low temperature range lignin in biomass forms some polymerization reaction which results in the formation of the resonance stabilized phenoxy radicals and some other reactive radicals. These radicals de-polymerize coal by splitting the methylene bridges. Such radicals are short lived as compared to the time required for complete depolymerization of coal[6, 7].

Walnut shells are agricultural biomass waste. According to STATISTA report the production of walnut in the world in 2019 is approximately 200000 metric tons [8]. The ratio of inner walnut to the outer shell is approximately 50% (by weight). Thus the approximate production of the shells is about 100 thousand metric tons. Although walnut shells are a valuable waste product and are present in large quantities, they are not widely used. Therefore, turning walnut shells into valuable products on an industrial scale is an important task.

Coal is ranked accordingly to the degree of that metamorphosis. Coal contains 60-95% carbonaceous contents and it also contains oxygen, sulfur, hydrogen and nitrogen [9]. But in co-pyrolysis with biomass, which acts as a hydrogen donor, the yield is improved. In composition coal and biomass are different, which is illustrated by Van Krevelen diagram with regards to hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios [10]. Biomass has higher H/C and O/C ratios as compared to coal. In co-pyrolysis conversion of coal can be facilitated by the oxygen content present in the biomass and increases the reactivity[11].Co-pyrolysis of biomass and coal goes through a series of complex reactions. The cellulosic materials (cellulose and hemicelluloses) decompose at lower temperature zone but lignin decomposes at higher temperature zone.

The purpose of this study is to pyrolyze a mixture of walnut shells and coal (local Makarwal coal) in a fixed bed reactor to study thermal decomposition at variable heating rates of 10, 20 and 25 °C/min and a temperature range of 300°C to 550 °C. To investigate the results of pyrolysis process [12], TGA was performed from ambient temperature to 950°C using the above mentioned heating rates. TG provides the thermal degradation information to understand the pyrolysis mechanism [13]. The pyrolysis process activation energy, found out by Flynn Wall Ozawa (FWO) and Kissinger (KAS) method, was predictedfrom the TGA data [14]. The biochar obtained during the pyrolysis process was characterized by proximate and CHNS analysis.

Materials and method

Walnut shells growing in the northern region of KPK Province, including the Malakand district, were taken as the source for this study, while the other material was the indigenous coal from the Makarwal coal field in Punjab. Walnut shell and the blend of walnut shell and coal were grounded inapebble mill, the pebble mill was used to tobring the walnut shell and charcoal mixture to the desired particle size. Prepared feedstock was pyrolyzed into the fixed bed reactor having a 14.2-inch-diameter fixed bed reactor equipped with a control panel to monitor the experimental readings.

To determine the thermal behavior and apparent activation energy, characteristics such as proximal, elemental, and TGA analyses of coal and walnut shell mixture with indigenous coal were performed using the Kissinger model (KAS) and the FWO method [5].

Kissinger Equation:

$\ln(\beta / T_m{}^2) = \ln(AR/E_a) - E_a/RT_\mathrm{m}$,

where T_m is the reaction exothermic peak temperature.The Kissinger method is based on a series of experiments on heating samples at several (always three or four) different heating rates using thermal analysis instruments such as DSC and DTA.[15]. Then the reaction exothermic peak temperature at each heating rate is recorded to calculate the kinetic parameters. For a thermal reaction, the rate of conversion can be described by two separate functions f(x) and k(T)

$dx/dt = f(x)k(T)$

Plot ln $(\beta/T_m{}^2)$ versus $1/T_m$ and fit all data using a straight line, then the slope (k) and the intercept (b) of the line equals to $-E_a/RT_m$ and $\ln(/E_a)$, respectively. Finally, the activation energy (Ea) can be obtained by -k multiply the gas constant R (8.314 J $\mathrm{mol^{-1}}$ $\mathrm{K^{-1}}$) and the Arrhenius pre-exponential factor (A) can be obtained by bE_a/R. On the basis of the Kissinger method [16], several other kinetic methods have also been developed, such as Kissinger Akahira-Sunose (KAS) method. The Ozawa method is another popular approach for determining kinetic parameters. It was developed by Takeo Ozawa in 1965. Similar as the Kissinger method, the Ozawa method also depends on a series of experiments that heating samples at several different heating rates. The kinetic parameters are also determinated by recording the reaction exothermic peak temperature at each heating rate [17]:

$log\beta = -0.4567\ E_a/RT - 2.315 + \log(AE_a/R) - \log[g(x)]$

Proximate analysis was performed in muffle furnace 48000, temperature range upto 1200 °C, elemental analysis was performed in CHNS-628 (LECO)[18]. A sample of walnut shells mixed with charcoal in a 50 : 50 ratio of 100 mg-250 mg is placed in a cup in the presence of carrier gas helium, oxygen and compressed air (used for a sample without oil and water) and a procedure for the detection of carbon, hydrogen and sulfur by non-dispersive infrared absorption and nitrogen by thermal conductivity detector. The elemental analyzer must be able to perform the analysis for carbon, hydrogen, nitrogen and sulfur simultaneously for 4-5minutes. Bomb calorimeter AC-500 used to calculate the calorific value of walnut shell and blend of walnut shell with coal[19, 20]. A Windows-based operating system uses an electronic thermometer with an accuracy of 0.0001°C to measure the temperature every six seconds. Results may be obtained using a choice inthree modes: the traditional = 20 minutes, precision = 8 minutes, or predictive = 4.5 to 7.5 minutes.Equipment name: TA INSTRUMENT SDT Q-600[21]. From 3 to 50 mg of a sample of walnut shells and a mixture of charcoal and walnut shells were placed in a platinum cup[22].

Experimental setup

Fixed bed reactor was used for recent experimental research along with suitable auxiliaries and accessories. Usually fixed bed reactors are installed because the installation of these reactors is easy to construct, control and maintain. Moreover, they provide an easy platform for the extension of the studies to pilot plant level.

A flange and head shall be fixated on cylinder so that a proper gas seal could be employed. Nitrogen purging is done at the top of the pyrolysis reactor, along with a provision of outlet point for removing pyrolysis fumes. A 12.5 inch long stainless steel capsule shall be installed in the center of the reactor to house the thermocouple. The inlet chute shall be inserted 11-inch insidethereactor to achieve a smooth flow of products and feed within the reactor. During a particular run, the capsule containing the thermocouple shall be in direct contact of the feed sample. Hence, accurate temperature readings are achieved. In order to maintain pressure in the reactor and avoid leakages, the reactor shall be sealed by use of silicon tubing and high temperature viton rubber seals/rings.

Experimental procedure

First, purge gas was fed to reduce the oxygen content at a rate of 0.2 L/min until the end of the experiment and placed 20 g of a mixture of walnut shells and coal (50 : 50) and again repeated the same procedure with a sample of walnut shells with a particle size of 0.210–0.500

mm in a fixed bed reactor. After half an hour, the electric panel was switched on and a constant supply of volts was maintained. The first experiment was conducted at 95 volts and a final temperature of 500 ^{0}C. The cooled water was fed inside the condenser tube, and the pyrolytic gases passed outside the condenser. The cooled water was fed through the water cooler continuously until the end of the release of gases from the reactor. When the desired temperature was reached, the electric heater was turned off and then the gas flow was run, after which the desired sample was collected and the yield weight was noted. The condensed gases are the main product of the pyrolysis of the walnut shell-coal mixture in this study. Similarly, another experiment was performed by varying the heating rates of 10, 20, and 25 °C/min.

Results and discussion

Table 1 shows the results of proximate analysis of raw materials - walnut shells and walnut mixture with local coal. The fixed carbon in the walnut shell is relatively lower than in the mixture, which means a high propensity for combustion, but an important factor determining the content of free and bound carbon. The moisture content directly affects the product and volatile substances, which decide how many fractions of the liquid product are formed. In addition, condensable and non-condensable substances can be measured if the temperature of the water feed into the condenser is controlled. The mixture has high ash content and high HHV due to the presence of carbon and hydrogen, which is 20.1 MJ/kg.

Table1

Proximate analysis of walnut shells andblend of walnut shells with coal

Sample	Fixed Carbon (%)	Moisture (%)	Volatile Matter (%)	Ash (%)	Calorific val (MJ/kg)
Walnut Shells	16.01	4.61	77.03	2.35	19.5
Walnut Shell Indigenous Coal	27.07	2.96	65.88	4.14	20.1

Table2 shows the results of CHNSanalysis of the walnut shells and the blend of walnut shells and indigenous coal. The sulfur content of the blend has a great influence on the product, but if a pre-treatment is done to remove the sulfur, the product should be economical, and another way to improve the composition of the walnut shells. In this analysis, the ratio of walnut shells to indigenous coal is 50 : 50.

Table2

CHNS analysis of walnut shells and coal

Sample	C	H	N	S
Walnut Shells	48.54	4.55	0.68	0.8
Walnut Shells& Indigenous Coal	55.5	6.85	2.83	4.4

Table 3 shows the biochemical analysis of walnut shells. It was observed that hemicelluloses decomposes at lower temperature from 200 to 320 °C, then cellulose contents in biomass decomposes at higher temperature from 300 to 400 ° Cbecause of high glucose contents and mostly liquid product produced when lignin,which consist of mostly ring and complex structures, also decompose at higher temperature of 200 to 500 °C which is responsible mostly for solid product.

Table 3

Biochemical analysis of walnut shells blend of walnut shell with indigenous coal

Sample	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Walnut Shells	27.4	31.3	36.31
Walnut Shell Indigenous Coal	16.4	22.3	27.31

*remaining Ash (%)

Figure1 shows the TGAanalysis of walnut shells and indigenous coal. Thermal degradation was investigated at three heating rates of 25, 20 and 10 °C/min. In the initial stage, increasing the temperature to 110°C removes the moisture content, followed by removal of volatile substances and primary cracking in the second stage of weight loss. Some of the char also decomposed and overlapped with volatile matters curve. At the high heating rate, a high decomposition rate of the material was observed and a mostly liquid product was obtained at 427 °C. In the third stage, decomposition due to secondary cracking was observed and mainly a gaseous product was obtained. In the fourth stage, when the weight loss curve became horizontal, no change was observed as all of the mixture material was converted into products. At the slow heating rate, it was observed that the final product formed mostly coal. Figure 3 shows the DTG result. At the high heating rate of 25 °C/min the conversion rate was also high.

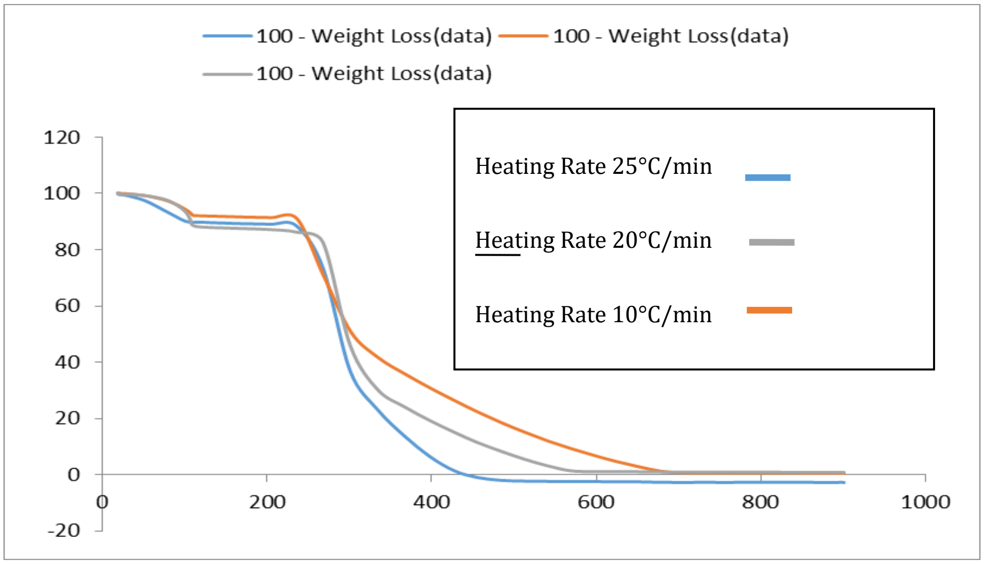


Fig.1. TG Aanalysis of blend of walnut shells and indigenous coal

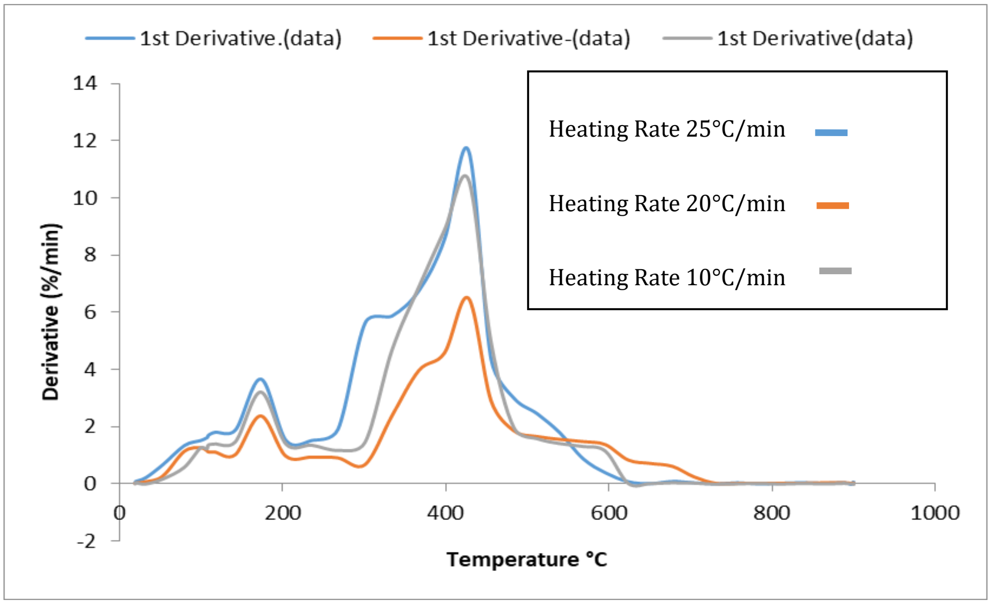


Fig. 2. DTG analysis of blend of walnutshells and indigenous coal

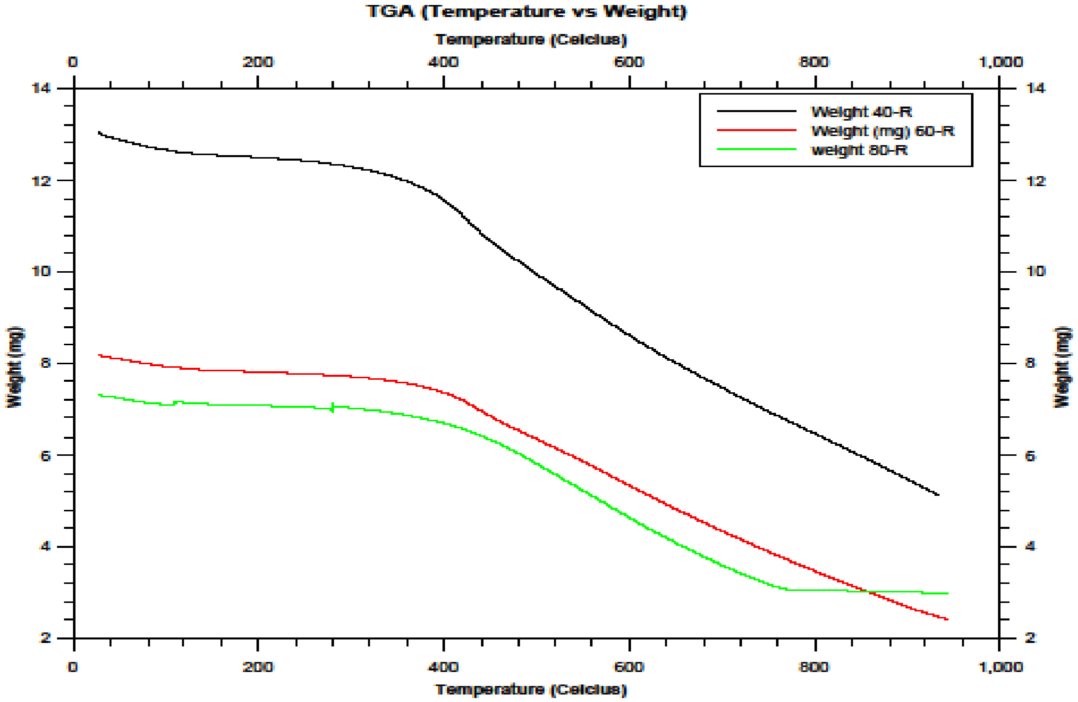


Fig. 3. TG Aanalysis of indigenous Makarwalcoal

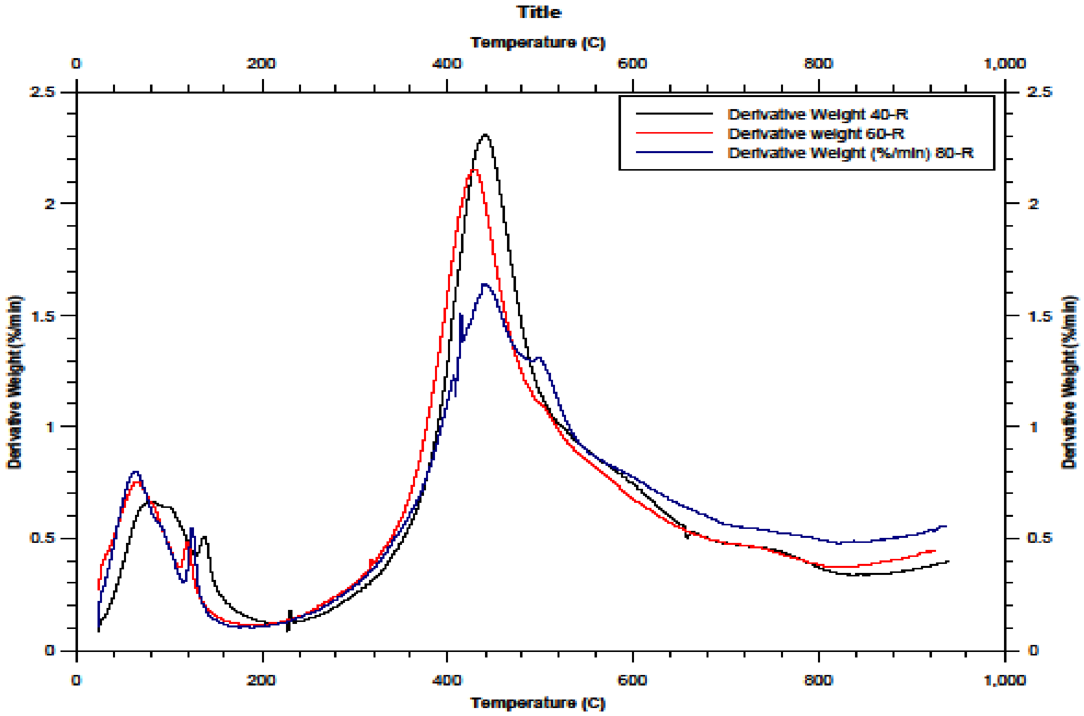


Fig. 4. DTG analysis of indigenous Makarwal coal

Table 4

Experimental results of blend of coal and walnut shells

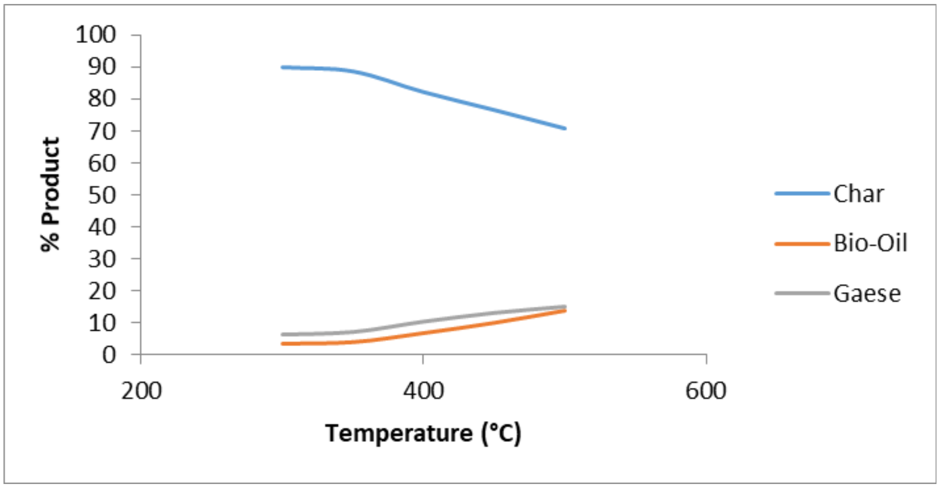
Temp (^{0}C)	Particle Size (mm)	Heating Rate (^{0}C/min)	%Yield of Charcoal	%Liquid Yield	%Gas Yield
300	0.5	10	90	3.5	6.5
350			88.7	4.0	7.3
400			82.2	6.9	10.5
450			76.6	10.2	13.2
500			70.8	14.1	15.1
300	0.297	20	72.4	5.7	21.9
350			70.9	7.9	37
400			55.1	20.4	24.5
450			50.3	24.2	25.5
500			42.9	20.1	63
300	0.21	25	69.4	6.3	24.3
350			66.2	8.5	25.28
400			45.6	21.5	32.9
450			40.1	26.4	33.5
500			38.7	21.4	39.9

Table 4 shows the experimental results of pyrolysis of the mixture. It was investigated that at high particle size and lower heating rate the gaseous and liquid product had little effect on char production. When the heating rate was increased to 20 °C/min and the particle size was reduced to 0.297 mm, a liquid product of 24.2 % was obtained. The particle size had little effect on the product selection. It was investigated that reducing the particle size to 0.21 mm and increasing the heating rate to 25 °C/min yielded a liquid product at 450 °C of 26.4 % and char of 40.1 %. The gases released during pyrolysis can be recycled if the product quality is improved.

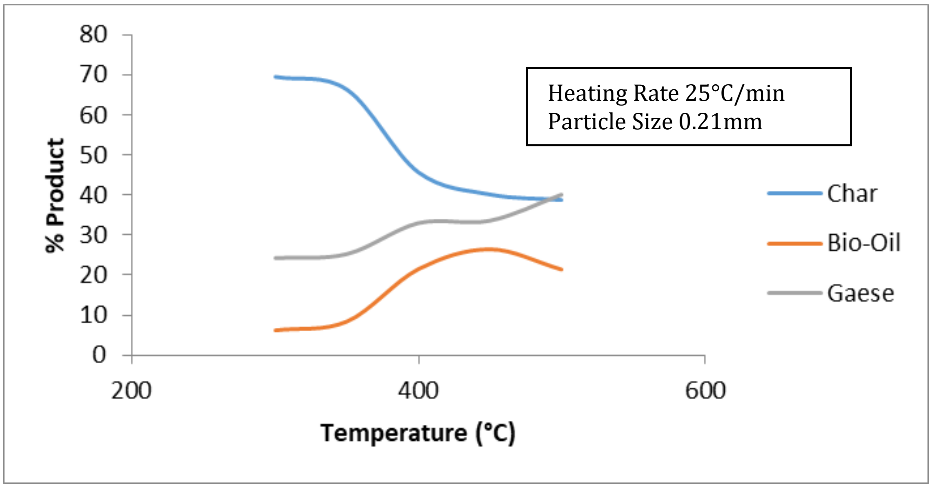
Figure 5 shows the results of extermination at a heating rate of 10°C/min, where it is investigated that at a low heating rate the primary cracking of the raw material is mainly converted into biochar production. In the transition to high temperature, when the heating rate remains constant, mostly gases are released due to the increase in volatility reaction and secondary cracking occurs. Figure 6 shows that at a high heating rate of 25 °C/min at a certain limit, the bio-oil yield was 26.4 %, after which most of the biochar was produced, as most of the volatiles were converted to condensable gases.

Figure 6(a) shows the result of the Kissinger method at heating rates of 10, 20, and 25 °C/min. It was investigated that the activation energy is obtained by the slope $-E_a/RT$, and the intercept y gives the value of the frequency factor (A). Figure 6(b) shows the result of the FWO method for finding the activation energy and frequency factor by adding the trend line method and equation giving the value of E_a and A.

Figures 8 and 9 show the spectrum of the Kissinger method and FWO. In this study, the conversion α increased from right to left in both figures, which means that when the conversion is low, three different values are obtained at different heating rates. At the lowest heating rate of 10 °C/min, the value of Ln (B/T^2) should be small, which increases as the heating rate increases from 20 °C/min to 25 °C/min. Similarly, in the FWO study, the gap between the lines initially increased from a conversion of 0.1, which means a high amount of absorbed energy at the lowest heating rate, little change was observed when the heating rate was increased with conversion α.



a



b

Fig. 5. % product obtained at heating rate of 10°C/min (a) and 25°C/min (b)

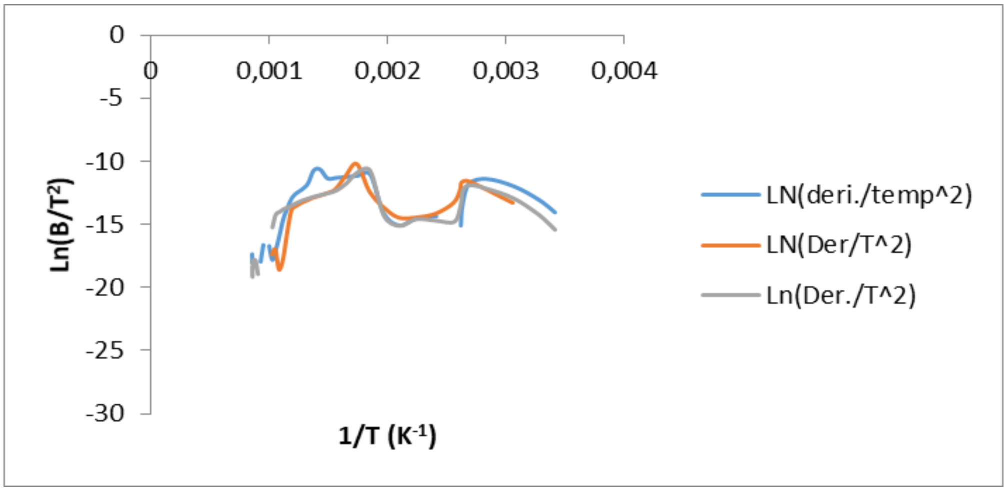


Fig. 6. KAS model for blend of coal and walnut shell

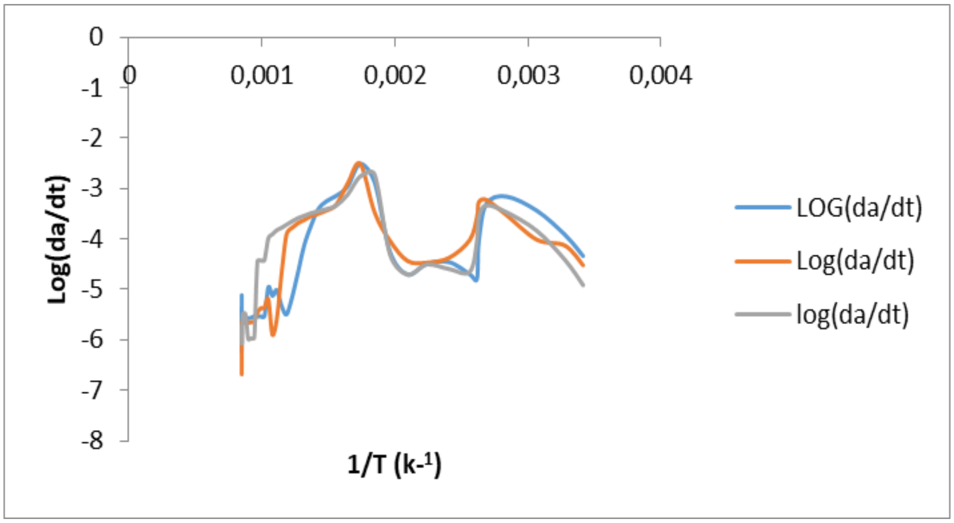


Fig. 7. FWO model for blend of coal and walnut shell

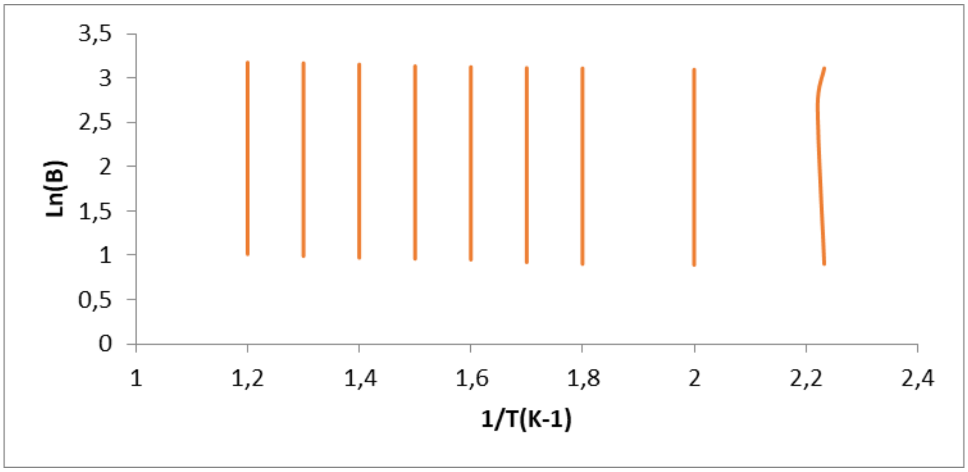


Fig. 8. FWO model for blend of coal and walnut shell to find the E_a

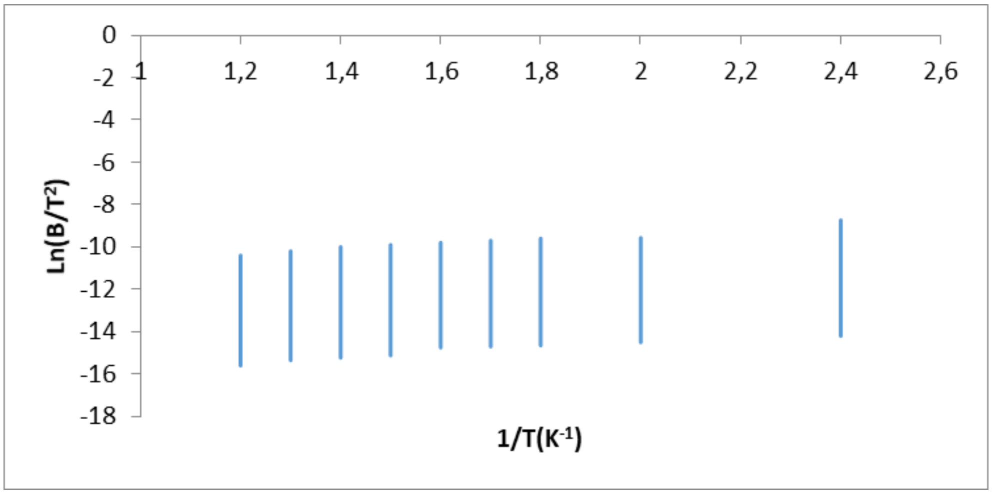


Fig. 9. KAS model for blend of coal and walnut shell to find the E_a

Table5

Observed from FWOmodel and KAS

Conversion	FWO		KAS	
	Ea(KJ/mol)	R	Ea(KJ/mol)	R
0.1	126	0.997	105	0.992
0.2	130	0.995	125	0.996
0.3	136	0.994	145	0.995
0.4	146	0.993	175	0.995
0.5	165	0.996	220	0.9954
0.6	190	0.959	270	0.997
0.7	120	0.950	210	0.993
0.8	85	0.990	180	0.991
0.9	110	0.965	120	0.990

Table 5 shows the activation energies of the two different methods. In the case of the FWO method, when the conversion was increased from 0.1 to 0.6, the E_a value increased and the highest value of 190 kJ/mol was obtained at 0.6 conversion ratio and the lowest at 0.1 conversion ratio. In the case of the Kissinger method, when the equation was applied at 0.6 conversion ratio, an E_a value of 270 kJ/mol was observed.

Table 6

Proximate and CHNS analysis of biochar product obtained from co-pyrolysis of walnut shells and indigenous coal

Sample	Fixed Carbon (%)	Moisture (%)	Volatile Matter (%)	Ash (%)	Calorific Value (MJ/kg)
Walnut Shell & Indigenous Coal	66.01	0.22	30.13	3.64	22.4
	C	**H**	**N**	**S**	
Walnut Shells & Indigenous Coal	69.45	9.42	1.60	0.85	

Table 6 shows the results of post-experimental analysis of the obtained biochar. The fixed carbon content, which directly affects the heating rate, increased to 66.01 %, and the volatile matter content decreased to 30.13 %, indicating that 70 % of the volatile matter from the raw material was converted to bio-oil and non-condensable gases. Elemental analysis of biochar showed that the percentage of carbon also increased, which can be used as fuel, most importantly, the sulfur content, which causes corrosion, decreased from 4.42% to 0.89%, which affects the environmental friendliness of the fuel.

Conclusions

Pakistani coal has a serious issue with its pre-treatment. That’s why the blend of coal and walnut shells is used in present research to utilize a large reserve of coal by means of walnut shells. The present study used a 50 : 50 ratio of both feedstocks, which were pyrolyzed in fixed bed reactor. The thermal degradation of the blend of walnut shells and coal was investigated by TGA and DTG analysis at different heating rate of 10, 20 and 25°C/min. At 427 °C and 25 °C/min, the maximum degradation of blend was observed, indicating that 26.4% of the bio-oil and 39% of the biochar fraction could be used for fuel. The minimum amount is preferred for the activation energy that is obtained at low conversion, and the highest amount of activation energy of 190 kJ/mol is obtained at a conversion of 0.6. The biochar obtained after pyrolysis of a mixture of walnut shells and charcoal was also characterized by proximate analysis, and elemental analysis showed that the sulfur fraction decreased from 4.48 % to 0.85 % and the heating value increased to 22.4 MJ/kg.

References

[1] Ghosh, S. K. (2016). Biomass & bio-waste supply chain sustainability for bio-energy and bio-fuel production, *Procedia Environmental Sciences,* 31, 31-39.

[2] Burra, K. R. G., Gupta, A. K. (2020). Nonlinear synergistic effects in thermochemical co-processing of wastes for sustainable energy, *Innovations in Sustainable Energy and Cleaner Environment*: Springer, 117–148.

[3] Vassilev, S. V., Vassileva, C. G., Vassilev, V. S. (2015). Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview, *Fuel,* 158, 330-350.

[4] Hu, J., Si, Y., Yang, H., Shao, J., Wang, X., Lei, T., Agblevor, F. A., Chen, H. (2017). Influence of volatiles-char interactions between coal and biomass on the volatiles released, resulting char structure and reactivity during co-pyrolysis, *Energy Conversion and Management,* 152, 229–238.

[5] Ren, X.-Y., Feng, X.-B., Cao, J.-P., Tang, W., Wang, Z.-H., Yang, Z., Zhao, J.-P., Zhang, L.-Y., Wang, Y.-J., Zhao, X.-Y. (2020). Catalytic conversion of coal and biomass volatiles: a review, *Energy & fuels,* 34, 10307–10363.

[6] Abdelsayed, V., Ellison, C. R., Trubetskaya, A., Smith, M. W., Shekhawat, D. (2019). Effect of microwave and thermal co-pyrolysis of low-rank coal and pine wood on product distributions and char structure, *Energy & fuels,* 33, 7069–7082.

[7] Wang, S., Dai, G., Yang, H., Luo, Z. (2017). Lignocellulosic biomass pyrolysis mechanism: a state-of-the-art review," *Progress in Energy and Combustion Science,* 62, 33–86.

[8] Sanchez, J., Curt, M. D., Robert, N., s. FernÃ¡ndez, J. (2019). Biomass resources, *The Role of Bioenergy in the Bioeconomy*: 25–111.

[9] Wang, X., Li, C., Li, Z., Yu, G., Wang, Y. (2012). Effect of pyrolysis temperature on characteristics, chemical speciation and risk evaluation of heavy metals in biochar derived from textile dyeing sludge," *Ecotoxicology and Environmental Safety,* 168, 45–52.

[10] Ravikiran, A., Renganathan, T., Pushpavanam, S., Voolapalli, R. K., Cho, Y. S. (2012). Generalized analysis of gasifier performance using equilibrium modeling, *Industrial & Engineering Chemistry Research,* 51, 1601–1611.

[11] Uzoejinwa, B. B., He, X., Wang, S., A. Abomohra, E.-F., Hu, Y., Wang, Q. (2018). Co-pyrolysis of biomass and waste plastics as a thermochemical conversion technology for high-grade biofuel production: Recent progress and future directions elsewhere worldwide," *Energy Conversion and Management,* 163, 468–492.

[12] Zanatta, E. R., Reinehr, T. O., Awadallak, J. A., Klein Ãbing, S. J., dos Santos, J. B. O., Bariccatti, R. A., Arroyo, P. A., da Silva, E. A. (2016). "Kinetic studies of thermal decomposition of sugarcane bagasse and cassava bagasse, *Journal of thermal analysis and calorimetry,* 125, 437–445.

[13] Sher, F., Iqbal, S. Z., Liu, H., Imran, M., Snape, C. E. (2020). Thermal and kinetic analysis of diverse biomass fuels under different reaction environment: A way forward to renewable energy sources, *Energy Conversion and Management,* 203, 112266.

[14] Singh, R. K., Pandey, D., Patil, T., Sawarkar, A. N. (2020). Pyrolysis of banana leaves biomass: Physico-chemical characterization, thermal decomposition behavior, kinetic and thermodynamic analyses, *Bioresource technology,* 310, 123464.

[15] Zhang, X. (2020). Applications of Kinetic Methods in Thermal Analysis: A Review, *Engineered Science,* 14, 1–13.

[16] Rony, A. H., Kong, L., Lu, W., Dejam, M., Adidharma, H., Gasem, K. A. M., Zheng, Y., Norton, U., Fan, M. (2019). Kinetics, thermodynamics, and physical characterization of corn stover (Zea mays) for solar biomass pyrolysis potential analysis," *Bioresource technology,* 284, 466–473.

[17] Burnham, A. K. (2017). Introduction to chemical kinetics, *Global Chemical Kinetics of Fossil Fuels*: Springer, 25–74.

[18] Donahue C. J., Rais, E. A. (2009). Proximate analysis of coal, *Journal of Chemical Education,* 86, 222.

[19] Overdeep, K. R., Weihs, T. P. (2015). Design and functionality of a high-sensitivity bomb calorimeter specialized for reactive metallic foils," *Journal of thermal analysis and calorimetry,* 122, 787–794.

[20] Hossain, N., Jalil, R. (2018). Analyses of bio-energy properties from Malaysian local plants: sentang and sesendok, *Asia Pacific Journal of Energy and Environment,* 5, 7–10.

[21] Halder, P., Kundu, S., Patel, S., Parthasarathy, R., Pramanik, B., Paz-Ferreiro, J., Shah, K. (2019). TGA-FTIR study on the slow pyrolysis of lignin and cellulose-rich fractions derived from imidazolium-based ionic liquid pre-treatment of sugarcane straw, *Energy Conversion and Management,* 200, 112067.

[22] Lecinena, M. (2020). Gas cleaning from sulfur-and nitrogen compounds of product gases from dual fluidized bed steam gasification via adsorption, Wien.