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Effects of green and innovative pretreatment techniques on kinetic parameters of sunflower seed husk

Yeşil ve yenilikçi ön işlem tekniklerinin ayçiçek çekirdek kabuğunun kinetik parametreleri üzerindeki etkileri

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Abstract

The effects of green pretreatment processes, such as ultrasonic process (US) and deep eutectic solvent (DES), applied to the biomass on kinetic parameters are as important as their effects on characteristic properties. Process conditions and course of reaction progression depend on the knowledge about kinetic parameters, activation energy and reaction model of thermal degradation in scale-up studies. Therefore, in this study, the change in the kinetic parameters with US applied with both distilled water and DES (glycerol:sodium acetate) at 100 W power and 20 kHz frequency for 10 minutes to sunflower seed husk (SSH) was revelaed. Isoconversional methods Kissinger-Akahira-Sunose (KAS) and Flynn- Wall-Ozawa (FWO) were preferred for the evaluation of activation energy of SSH and pretreated SSH at 15°C/min, 20°C/min and 25°C/min heating rates. US pretreatment with DES instead of water resulted in increment of average activation energy values (E_a) from 113.13 to 143.65 kJ/mol in the KAS method. Ea values for all SSH samples changed in the range of 87.72-143.65 kJ/mol and higher Ea values was obtained with KAS method for pretreated SSH samples. Consequently, the use of DES in US pretreatment was more effective to change kinetic parameters of SSH compared to water.

Keywords: Deep eutectic solvents, Green technologies, Kinetic modelling, Sunflower seed husk, Ultrasonic process

Öz

Biyokütleye uygulanan ultrasonik proses (US) ve derin ötektik çözücü (DES) gibi yeşil ön işlem proseslerinin karakteristik özellikler üzerindeki etkileri kadar kinetik parametreler üzerindeki etkileri de önemlidir. Proses koşulları ve reaksiyon ilerlemesinin seyri, ölçek büyütme çalışmalarında kinetik parametreler, aktivasyon enerjisi ve termal bozunmanın reaksiyon modeli hakkındaki bilgilere bağlıdır. Bu nedenle bu çalışmada ayçiçek çekirdek kabuğuna (SSH) 100 W güçte ve 20 kHz frekansta 10 dakika süreyle hem distile su hem de DES (gliserol:sodyum asetat) ile uygulanan US prosesi ile kinetik parametrelerdeki değişim ortaya konmuştur. 15°C/dk, 20°C/dk ve 25°C/dk ısıtma hızlarında SSH ve ön işlem görmüş SSH'nin aktivasyon enerjisinin değerlendirilmesinde Kissinger-Akahira-Sunose (KAS) ve Flynn-Wall-Ozawa (FWO) izokonversiyonel yöntemler tercih edilmiştir. US'de su yerine DES ile yapılan ön işlem, KAS yönteminde ortalama aktivasyon enerjisi değerinin (Ea) 113,13'ten 143,65 kJ/mol'e yükselmesine neden olmuştur. Tüm SSH numuneleri için Ea değerleri 87,72-143,65 kJ/mol aralığında değişmiş ve ön işlem görmüş SSH numuneleri için KAS yöntemi ile daha yüksek E_a değerleri elde edilmiştir. Sonuç olarak, US ön işleminde DES kullanımı, suya kıyasla SSH'nin kinetik parametreleri üzerinde daha etkili olmuştur.

Anahtar kelimeler: *Derin ötektik çözücüler, Yeşil teknoloji, Kinetik modelleme, Ayçiçek çekirdek kabuğu, Ultrasonik proses*

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1. Introduction

Sunflower is widely cultivated in all over the world due to the high resistance to the environmental conditions., e.g.it is production ratio is nearly 50 million tons/year for European countries. Correspondingly, millions of sunflower seed husk (SSH) is produced every year since 30-50% of the seed is husk (Perea-Moreno et al., 2018; Gandariasbeitia et al., 2022). It commonly uses to produce animal feed and its usage for energy purposes is very limited (Cui et al., 2019). However, SSH is one of the lignocellulosic biomasses having important carbon source and high energy content. Perea-Moreno et al., (2018) emphasized that SSH can be used effectively instead of fossil fuels, and it is important material for combustion applications. Similarly, Spirchez et al., (2019) proved that SSH is cheap, suitable, and promising lignocellulosic material as solid fuel by discussing durability and density of SSH. Additionally, SSH can be safer fuel comparing to the natural gas in terms of environmental aspect since it diminishes emissions of some pollutants such as suspended solids, volatile organic compounds, and methane (Horák et al., 2023). SSH can also be evaluated in different biomass conversion technologies such as thermochemical process, anaerobic treatment, chemical and physicochemical processes to obtain economically valuable products (Flores et al., 2021). However, most of these processes need pretreatment step to improve selectivity and conversion ratio of biomasses. Nowadays, ultrasonic-assisted (US) and deep eutectic solvents (DES) pretreatment methods are gaining importance since they have many advantages over the traditional methods. US can change physicochemical structure of lignocellulosic biomasses by disruption of lignin barrier, decreasing hemicellulose content and thereby increment in cellulose accessibility. It can also increase heat transfer, contact of the products and reactants (He et al., 2017). Moreover, US is a more environmentally friendly and economical application compared to traditional pretreatment methods since conventional methods are mostly required long time, high quantity of chemicals and high pressure/temperature (He et al., 2017). As for DES, they are green, easily recovered solutions, non-toxic for environment, biodegradable and high stabile comparing to the conventional chemical solvents (Alvarez-Vasco et al., 2016). They are produced based on H-bond formation between at least two components and can be used in many different application studies such as extraction process, pretreatment for lignocellulosic biomasses, using with other pretreatment systems (US, radiation etc.) (Li et al., 2022). DES can be prepared by using many different green solvents which one of these are hydrogen bond donor (HBD) and the other is hydrogen bond acceptor (HBA). Nowadays, interest in glycerol as HBD in the preparation of DES solutions has been increasing. Glycerol based DES solutions are being effectively used in the pretreatment process and/or extraction process such as polyphenol extraction. Mouratoglou et al., (2016) illustrated that glycerol-sodium acetate or sodium potassium tartrate outperformed as compared to water and ethanol during the extraction process of polyphenols. In literature, most of the studies are about the effects of these pretreatment process on characteristics of lignocellulosic biomasses (He et al., 2017; Li et al., 2023). For instance, Baksi et al., (2018) found that 85% lignin removal from *Crotalaria juncea* biomass was achieved with US treatment with water. Similarly, Subhedar & Gogate, (2014) emphasized that treated newspaper waste with US at alkaline conditions had lower lignin content than original form. In another study showed that crystallinity and molecular weight decreased with US pretreatment at 37 kHz and 150 W (Wong et al., 2012).

Mainly two-step process exists for kinetic analysis: experiments conducted at different temperatures or heating programs (isothermal or nonisothermal) and mathematical determination of kinetic parameters with model fitting, single-heating-rate methods, and isoconversional methods. The activation energy (E_a) of lignocellulosic biomass highly depended on the kinetic model. Ea values for sugar cane bagasse with Kissinger-Akahira-Sunose (KAS), Flynn- Wall-Ozawa (FWO) and Friedman method was found as 52.3, 61.7 and 127.7 kJ/mol, respectively (Gai et al., 2013). As for untreated and treated rice husk, Ea values was specified as 222.18, 227.98 kJ/mol in KAS model, 219.67, 218.83 kJ/mol in the FWO model (Kumar et al., 2020). Among kinetic models, many researchers prefer isoconversional methods, such as FWO and KAS model, since it has a foremost advantage compared to model-fitting and single-heating-rate methods and it is more suitable for complex materials, like biomass (Dhyani & Bhaskar, 2018). FWO method is applied for the calculation of activation energy via TGA analysis at constant heating rates. The activation energy is calculated from the slope of the graph of lnβ versus 1/T. As for KAS, it is differential method formulated by using Arrhenius equation. The slope of the ln (β/T^2) versus 1/T graph gives the $-E_a/R$ values (Sarkar & Wang, 2020).

In the literature, although several studies exist about the change of the characteristics of biomasses with US and DES pretreatment, limited studies have been performed by effects of these new pretreatment methods on kinetic parameters of biomasses. However, effects of US and DES pretreatment methods on kinetic parameters have also vital importance since they are required in scale-up studies. Kinetic studies have critical importance

for understanding course of reaction progression and to determinate the dependence of the rate of progression on process parameters. Moreover, establishment of process conditions depended on the knowledge about kinetic parameters, activation energy and reaction model of thermal degradation (Dhyani & Bhaskar, 2018). Thermogravimetric analysis (TGA) is commonly used for thermal degradation analysis of lignocellulosic biomasses. Moreover, TGA can be used for evaluation of reaction kinetics formulation, organic and inorganic content decision, characteristic decomposition patterns etc. (García et al., 2014; Manara et al., 2015; Ghouma et al., 2017; Dhyani & Bhaskar, 2018). Therefore, in the presented study, the effects of US pretreatment process conducted with both water and glycerol:sodium acetate DES solution on thermal characteristics and kinetic parameters of sunflower seed husk by using KAS and FWO method.

2. Material and method

Preparation of SSH sample

Sunflower seed husk (SSH) were taken from the facility of sunflower seed oil in Edirne/Türkiye, they were grinded and sieved to obtain SSH sample with the size of less than 300 micron.

Pretreatment of SSH sample

Ultrasonic (US) pretreatment was applied to the SSH sample with both distilled water and deep eutectic solvents (DES) solution. US pretreatment was conducted with Bandelin HD 3200 model US homogenizer and TT 13 model titanium probe. US process conditions were settled as 100 W power, 20 kHz frequency and 10 minutes processing time. In the literature, US process for lignocellulosic biomasses were applied mostly at 100 W power, 20-35 kHz frequency and for 10-60 minutes to obtain a remarkable effect on biomass characterization (Santos et al., 2020; Schmitz et al., 2021). Therefore, the experimental conditions in the presented study were chosen accordingly. The values for frequency and processing time were preferred as low as possible in terms of energy saving. The detail information about US preprocessing to the SSH samples was presented in Figure 1.

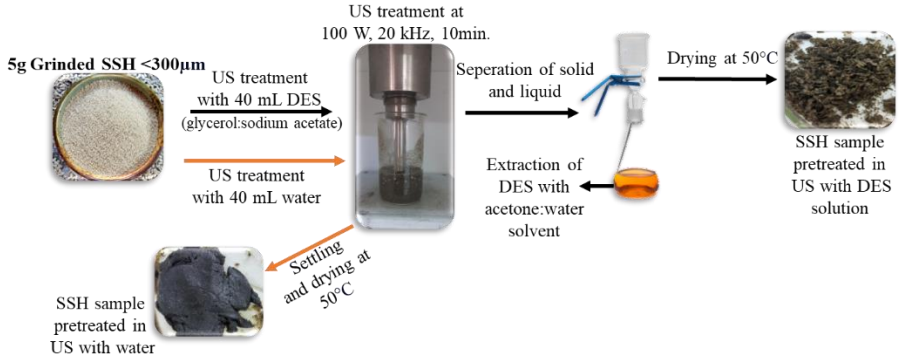

Figure 1. Ultrasonic pretreatment of SSH sample with water and DES solution

DES solution was prepared with the mixing sodium acetate:glycerol (molar ratio, 1:9) at 70°C until obtaining clear solvent mixture. Although DES solution with different molar ratios (such as 1:3, 1:5) for sodium acetate:glycerol was prepared, transparent solvent mixture was achieved with molar ratio of 1:9. DES solution was removed with acetone:water (1:1 v/v) mixture as anti-solvent after US preprocessing of SSH with DES solution as shown in Figure 1.

Kinetic modelling

Thermal analysis of SSH and pretreated SSH samples was conducted with Perkin-Elmer TGA4000 Model instrument at four different heating rate (15°C/min, 20°C/min, 25°C/min and 30°C/min; processing time 60 min., 45 min., 36 min., 30 min., respectively) and 900°C target temperature. Nitrogen gas was used at a ratio of 20mL/min to achieve an oxygen-free environment during TGA analysis.

TGA is effective and commonly used method for non-isothermal pyrolysis process for biomass (Sarkar & Wang, 2020). TGA process is conducted at constant heating rate and the conversion rate of biomass is expressed as (equation 1) where, m_i and m_f: initial and final mass of the sample, respectively; m_a: mass of the sample at any time during TGA analysis:

$$\alpha=\frac{m_i-m_a}{m_i-m_f} \quad (1)$$

KAS and FWO isoconversional methods were used for kinetic study of SSH and pretreated SSH samples for description of complex reaction mechanism and equations were given for these methods as follows (Zha et al., 2023):

$$\text{KAS: } \ln\left(\frac{\beta}{T^2}\right)=\ln\left(\frac{AR}{E_a G(\alpha)}\right)-\frac{Ea}{RT} \quad (2)$$

$$\text{FWO: } \ln(\beta)=\ln\left(\frac{AR}{E_a G(\alpha)}\right)-5.331-1.052\frac{Ea}{RT} \quad (3)$$

where, β=heating rate, T=temperature, R=gas constant, A= pre-exponential factor

3. Results and discussion

Thermal characteristics of SSH sample was given in Figure 2 for different heating rates. According to figure, mainly three degradation zones were observed. The first zone was the moisture evaporation between the temperature of 70°C -150°C. The second zone where the most degradation was observed due to the cellulose and hemicellulose degradation were between the temperature of nearly 220°C-350°C (Figure 2). More than 50% of the initial mass of SSH was degraded up to 400°C since the main portion of the SSH sample is cellulose and hemicellulose as specified in the studies (Demirbas, 2002; Kamireddy et al., 2014). Lignin has wide decomposition temperature range as compared to the cellulose and hemicellulose. It starts to degrade at 200°C with first pyrolysis reactions and it continues to degrade at temperature higher than 400°C with secondary pyrolysis reactions (Kawamoto, 2017). Therefore, the third zone (>400°C) observed in the Figure 2 belonged to the lignin degradation. Although the temperature observed the maximum degradation of SSH was very close to each other for different heating rates, maximum degradation temperature shifted right at 30°C/min heating rate condition (Figure 2). This can be attributed to the higher residence time for the sample in lower heating rate conditions. This higher residence time provides penetration of thermal gradients up to particles inner cores thereby this changes the maximum degradation temperature (Patidar et al., 2022).

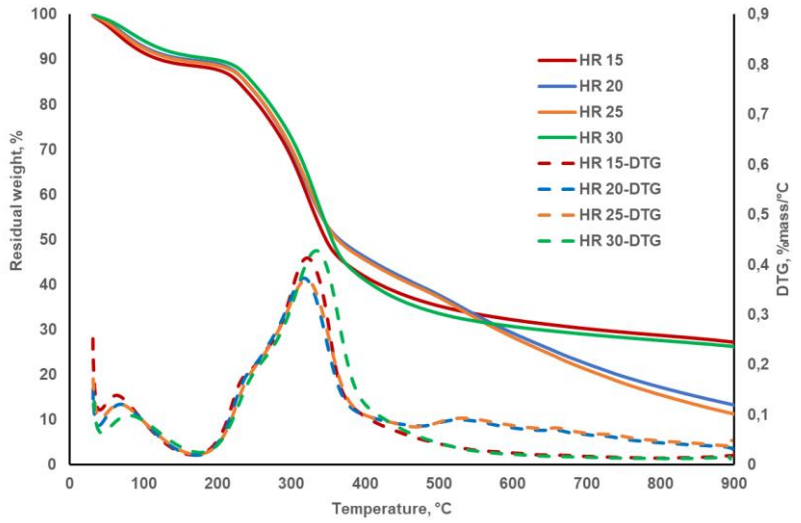

Figure 2. Thermal characteristics of SSH sample at different heating rate (Differential thermogravimetric analysis: DTG; HR: heating rate (°C/min))

Effect of ultrasonic pretreatment with distilled water and DES solution on conversion rate of SSH was compared in Figure 3. Both SSH and pretreated SSH samples had sigmoid shape curves for all heating rates. In the TGA analysis, short reaction time is needed for higher heating rate therefore degradation temperature for sample is also higher. Therefore, the higher temperature was needed at high heating rate for same mass conversion rates and therefore, curves mostly shifted to the right side from low to high heating rates (Figure 3(a-c)). This result is comparable with the other studies. Patidar et al., (2022) emphasized that lower temperature is needed at 5°C/min heating rate as compared to the 10°C/min and 20°C/min heating rates for

the same mass conversion rates. US pretreatment process with both water and DES affected mass conversion rate of SSH (Figure 3(d)). This can be explained with that both DES solution and US process have an important impact on the fractions of lignocellulosic biomasses. Lignin and hemicellulose fraction of lignocellulosic biomasses mostly decreased after US process with both DES and water as specified in the literature (Subhedar & Gogate, 2014; He et al., 2017). As seen in Figure 3 (d), DES solution usage during the US process instead of water highly affected mass conversion rate of SSH. Higher mass conversion rates were observed at much lower temperatures in pretreated SSH sample in US with DES. This is most likely due to the fact that the lignin fraction in the SSH structure is dissolved and/or reduced by DES during US preprocessing.

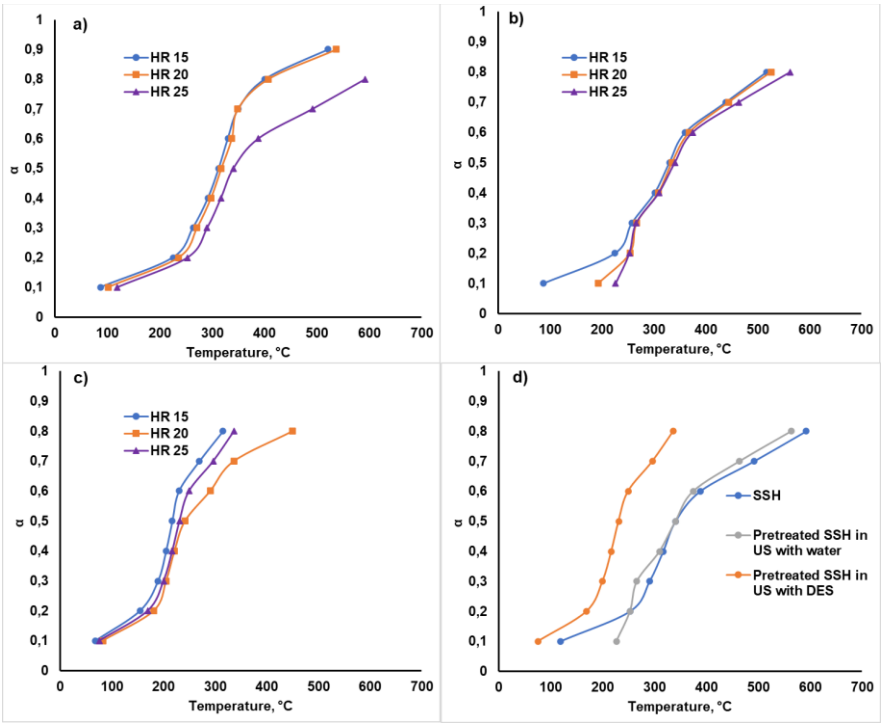

Figure 3. Mass conversion rate of SSH at different heating rates a) SSH, b) Pretreated SSH in US with water, c) Pretreated SSH in US with DES, d) SSH and pretreated SSH at 25°C/min heating rate

Activation energy for both SSH and pretreated SSH samples were calculated with model free methods of FWO and KAS by using equation 2 and 3 (Table 1 and Figure 4). Activation energy values calculated at conversion value of 0.1 were not used during fitting of data in models since correlation value for α=0.1 was low. Correlation value for other conversion values were higher than the 0.95. Although the average activation energy values calculated with FWO and KAS method were close to each other for SSH sample, higher activation values were obtained with KAS method for pretreated SSH samples (Table 1).

Table 1. Activation energy values calculated from KAS and FWO method with fitted equation for SSH and pretreated SSH samples

α	SSH		Pretreated SSH in US with water		Pretreated SSH in US with DES	
	E_a (kJ/mol)		E_a (kJ/mol)		E_a (kJ/mol)	
	FWO	KAS	FWO	KAS	FWO	KAS
0.2	68.45	53.75	29.10	19.07	91.02	156.00
0.3	94.99	81.77	99.09	106.97	134.78	177.20
0.4	120.62	108.69	152.02	183.51	125.32	155.90
0.5	151.58	141.20	147.49	192.48	177.89	213.11
0.6	168.30	158.70	120.81	151.54	104.56	112.66
0.7	157.83	147.57	76.03	95.44	87.54	107.68
0.8	104.21	128.45	50.75	56.61	83.41	100.25
0.9	61.66	84.94	26.48	16.80	74.63	126.38
Average	115.95	113.13	87.72	115.09	109.89	143.65

The average activation energy values from KAS were 113.13;115.09;143.65 for SSH, pretreated SSH in US with water and pretreated SSH in US with DES, respectively. Activation energy values calculated with KAS and FWO method for different biomass samples, such as coffee husks, cherry, and peach seed etc., were presented in the literature. Activation energy of most of these biomasses ranged between 74-288 kJ/mol (Coruh & Bayrakceken, 2020). Therefore, it can be indicated that presented activation values in this study coincide with the literature values.

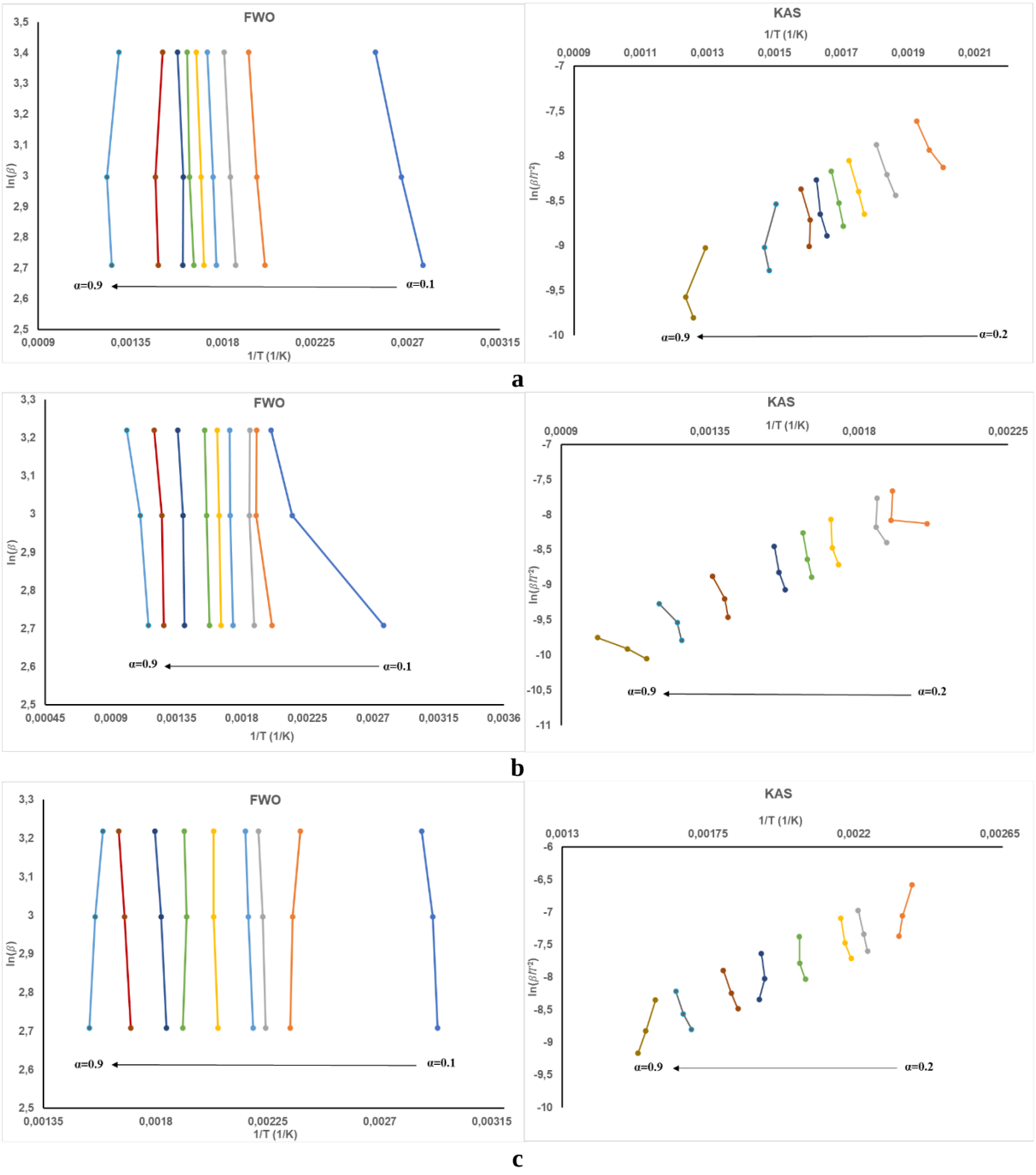

Figure 4. FWO and KAS method for evaluation of E_a a) SSH, b) Pretreated SSH in US with water, c) Pretreated SSH in US with DES

It has been noticed that a fluctuation exists in the activation energy based on conversion ratio for all SSH samples (Table 1). This fluctuation can be related to the thermal degradation of biomass components such as cellulose, hemicellulose and lignin content. Moreover, this fluctuation observed in activation energy values with conversion rate can be an indication that multiple reaction mechanism occurred during the pyrolysis of all SSH samples (Coruh & Bayrakceken, 2020). Additionally, an increment was observed in activation value

with US pretreatment, especially for KAS method. Santos et al., (2020) stated that activation energy for guava slices increased from 31.8 kJ/mol to 56.87 kJ/mol after 10 minutes US pretreatment. This can be related to the pretreated SSH samples with US need more energy for the initiation of diffusion process (Santos et al., 2020). Moreover, the different model free methods gave slightly different E_a values for pretreated SSH. This situation can be explained by the fact that the energy required for the initiation of the reaction (E_a) of treated SSH is more affected from the equations of the integral calculated with different approaches compared to untreated SSH due to the possible changes in the fractions of SSH. To conclude, it can be emphasized that US pretreatment with both water and DES had notable impact on thermal properties of SSH samples.

Kinetic parameters play a key role in the biomass conversion technologies to control product yield and correct design. Moreover, kinetic parameters should be taken into account for application and improvement of the biomass conversion technologies. Therefore, in this study, it was focused on the effects of the green and innovative pretreatment techniques on kinetic parameters of SSH. Increment in the activation energy value after pretreatment with green technologies is quite important result of the presented study; since it can be an indicator that pretreated SSH can have slow reaction rate comparing to SSH. Obtained results also shows that green technologies can be used effectively to change cellulose, hemicellulose, and lignin fractions of lignocellulosic biomasses for different purposes.

4. Conclusions

Ultrasonic pretreatment process was applied to the sunflower seed husk (SSH) with distilled water and glycerol:sodium acetate deep eutectic solvent (DES) as green solvent to evaluate the effects of these pretreatment process on kinetic parameters of SSH. The obtained results were specified as follows:

- Approximately 50% of the initial mass of SSH were degraded up to 400°C due to the high fraction of hemicellulose and cellulose.
- Higher residence time during the TGA analysis affected the maximum degradation temperature of SSH.
- Although the activation energy value calculated by both the FWO and KAS method was close to each other for the SSH sample, there was a remarkable difference for the pretreated SSH samples.
-Mass conversion rate and activation energy values of SSH sample changed prominently with ultrasonic pretreatment process with DES solution.
-The highest activation energy value (~144 kJ/mol) was observed for pretreated SSH in US with DES in the KAS method.

Consequently, KAS and FWO method can be effectively used to explain kinetic modelling of both SSH and pretreated SSH samples since correlation values of these methods were high. Mass conversion rate and kinetic modelling of SSH samples were highly affected with DES solution during the ultrasonic pretreatment process.

Author contribution
The entire article was written by the corresponding author.

Declaration of ethical code
The author of this article declares that the materials and methods used in this study do not require ethical committee approval and/or legal-specific permission.

Conflicts of interest
The author declares that there is no conflict of interest.

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