



Kinetic and analytical studies on pyrolysis of olive oil industry wastes

Gözde DUMAN TAC*

Department of Chemistry, Faculty of Science, Ege University, Izmir, Turkey

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*Corresponding author e-mail: gozdeduman@gmail.com

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ABSTRACT

The pyrolysis of olive pomace was carried out at two different heating rates at 500°C in the absence and presence of catalysts (commercial fluid catalytic cracking (FCC), aluminosilicate zeolite (ZSM-5) and red mud) using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The products obtained from biomass components in different temperature ranges by sequential pyrolysis of olive pomace were investigated. In addition, the apparent activation energy of olive pomace was calculated by thermogravimetric analysis method and determined as 105.6 kJ mole⁻¹ by Kissinger-Akahira-Sunose (KAS) method and 110.2 kJ mole⁻¹ by Flynn-Wall-Ozawa (FWO) method. According to Py-GC/MS results, the main components in bio-oil consists of phenolic compounds. In sequential pyrolysis, while the highest organic acid was obtained at low temperatures, phenolic compounds were formed at high temperatures. While bio-oil obtained by fast pyrolysis has higher organic acid content than that of bio-oil obtained by slow pyrolysis, slow pyrolysis bio-oil contains more furan and aliphatic ketone, aldehyde and ester. Catalytic studies revealed that catalysts were more effective in the slow pyrolysis process, which allows prolonged catalyst-pyrolysis vapor contact.

Keywords: Pyrolysis, TGA, Py-GC/MS, olive pomace waste, catalyst.

Zeytinyağı endüstrisi atıklarının pirolizi üzerine kinetik ve analitik çalışma

ÖZ

Piroliz gaz kromatografisi/kütle spektrometresi (Py-GC/MS) kullanılarak, pirinanın iki farklı ısıtma hızında 500°C'de katalizör yokluğunda ve varlığında (ticari akışkan katalitik çatlama (FCC), alimünosilikat zeolit (ZSM-5) ve kırmızı çamur) pirolizi gerçekleştirildi. Pirinanın basamaklı pirolizi ile farklı sıcaklık aralıklarındaki biyokütle bileşenlerinden elde edilen ürünler incelendi. Ayrıca pirinanın gözlenen aktivasyon enerjisi termogravimetrik analiz yöntemiyle hesaplandı ve Kissinger-Akahira-Sunose (KAS) metoduna göre 105.6 kJ mole⁻¹, Flynn-Wall-Ozawa (FWO) metoduna göre ise 110.2 kJ mole⁻¹ olarak belirlendi. Py-GC/MS sonuçlarına göre biyoyağın içindeki başlıca bileşenler fenolik bileşiklerden oluşmaktadır. Basamaklı pirolizde, en yüksek organik asit içeriği düşük sıcaklıklarda elde edilirken fenolik bileşikler yüksek sıcaklıklarda oluşmuştur. Hızlı piroliz ile elde edilen biyo-yağ, yavaş piroliz ile elde edilen biyo-yağdan daha yüksek organik asit içeriğine sahipken, yavaş piroliz biyo-yağı daha fazla furan ve alifatik keton, aldehit ve ester içermektedir. Katalitik çalışmalar, katalizörlerin, uzun süreli katalizör-piroliz buhar temasına izin veren yavaş piroliz işleminde daha etkili olduğunu ortaya koymuştur.

Anahtar Kelimeler: Piroliz, TGA, Py-GC/MS, pirina atığı, katalizör.

1. INTRODUCTION

Due to the depletion of fossil fuels and their environmental impact, renewables resources have been sought in recent years. Biomass materials are an abundant resource that is widely spread all around the world as well as the only carbon source among the other renewable resources. Although biomass materials are generally used as solid fuel in traditional methods, different conversion technologies have been developed to use biomass more efficiently and environmentally.¹

Among them, pyrolysis is one of the well-known thermochemical methods for converting biomass into value-added products in absence of oxygen. The yield and quality of the resultant products strongly depend on the conditions of pyrolysis as well as biomass type. Biomass consists of three major components, namely cellulose hemicellulose and lignin, and also relatively small amount of ash and extractives. Each component of biomass has different degradation routes during pyrolysis, giving different products. Basically, a high amount of solid product, so-called "biochar", can be

produced at low temperature pyrolysis and heating rates, while fast heating rate and high temperatures prefer the High yield of liquid products (bio-oil). Bio-oil is a mixture of more than hundred oxygenated organic compounds and has low quality in terms of fuel properties such as poor stability, low pH, high water content and viscosity etc. In order to improve its quality, bio-oil can be upgraded via heterogeneous catalysis. The main purpose of the upgrade is to obtain bio-oil with high energy content and stability by lowering the oxygen content of the bio-oil. Upgrading process can be applied in two ways, in-situ and ex-situ. These two processes distinguish between each other based on placement of the catalyst, as into the pyrolysis reactor or as separate reactor. There have been several studies on ex situ and in situ upgrading of bio-oil in presence of heterogeneous catalysts such as zeolites, metal oxides, etc.²

Besides these parameters, pyrolysis design is also effective on the characteristic of bio-oil. Bio-oil obtained from lab-scale pyrolysis systems probably depends on the pyrolysis unit, recovery and characterization methods. Therefore, a reliable data comparison, which is independent from reactor design, is required to investigate the effect of various conditions such as heating rate, temperature, the presence of catalyst, etc. on bio-oil composition. For this purpose, pyrolysis coupled with gas chromatographic separation and mass spectrometry detection is being used to provide preliminary chemical information on potential compounds derived from bio-oil.³ This system is called pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Py-GC/MS offers repeatable and rapid chromatographic separation with using small quantities of sample. Several works have been performed to investigate the pyrolysis parameters such as temperature,⁴ heating rate,⁵ biomass type,^{6,7} particle size,⁸ catalyst⁹⁻¹³, and catalyst contact type¹⁴ on bio-oil composition.

Thermogravimetric analysis is another technique for investigating the pyrolysis behavior of biomass by determining kinetic parameters that provide useful information for pyrolysis parameter optimization and reactor design. Kinetic studies can be performed by two methods, isothermal and non-isothermal model. Non-isothermal method is widely used due to elimination of systematic errors arisen from unfitting assumptions of the reaction mechanism.¹⁵ On the other hand, biomass pyrolysis involves very complex and competitive reactions that cannot be expressed by simple mechanism pathways. At this point, the model-independent approach, that is, the iso-transform method, gives more reliable results in determining the kinetic parameters.¹⁶ Basically, iso-conversional method is calculated as a function of the extent of conversion at different heating rates. Kissinger-Akahira-Sunose

(KAS) and Ozawa-Flynn-Wall (OFW) are the examples of iso-conversional models based on integral approach for TGA data processing.

Mediterranean countries have an important potential in the olive oil sector by producing 97% of the world's olive oil production.¹⁷ Over the past five years, olive oil production in Turkey has increased by 20% and reached the second highest level in 2019 production with annual production of approximately 200,000 tons.¹⁸ A large amount of olive pomace are produced from olive oil extraction by the olive oil sector. Depending on the manufacturing process, olive pomace contains 45-70% of moisture. Olive pomace is usually treated with organic solvents to extract the residual oil, which is called pomace oil.

In this study, pyrolysis of olive pomace after solvent extraction was conducted under various conditions by using Py-GC/MS. Thermal degradation of olive pomace was analyzed using thermogravimetric method in order to determine apparent activation energy. Thermal and catalytic pyrolysis experiments were performed at slow (25°C/min) and fast (1200°C/min) heating rates in order to investigate the effect of catalysts on bio-oil composition. Sequential pyrolysis was also carried out to determine the change in chemical compounds in bio-oil as a function of biomass components.

2. MATERIALS AND METHODS

2.1. Material

Olive pomace, a byproduct of olive oil company, was supplied from olive pomace oil company in Izmir city, Turkey. Olive pomace was dried at 105°C overnight, it was grinded to a particle size less than 250 μ m and stored in sealed glass bottles until its use. Ultimate analysis was carried out using LECO CHNS 932 elemental analyzer according to ASTM D5291-96. The proximate analysis was done according to NREL/TP-510-42622 and ASTM D3175-89a for ash and volatile matter, respectively. The procedure reported by Li and co-workers¹⁹ was followed to determine the components of olive pomace. Proximate, ultimate and component analyses were performed in duplicate to ensure reproducibility of the characterization results. Relative deviation of the analyses was found to be less than 5%. The properties of olive pomace are given in Table 1.

Three different catalysts were tested in catalytic pyrolysis run. ZSM-5 is sodium aluminosilicate zeolite, which is commercially available (Zeolyst International). Fluid catalytic cracking (FCC) is commonly used in petroleum refineries for conversion of crude oils into more valuable products such as gasoline, olefinic gases, etc. Commercial FCC was provided from Izmir Refinery, Turkey.

Table 1. Properties of olive pomace

Proximate analysis		(wt%)
Moisture		8.1
Volatile matter		69.5
Fixed carbon		19.1
Ash		3.3
GCV, MJ kg ⁻¹		20.6
Ultimate analysis (dried weight)		(wt%)
C		50.6
H		5.9
N		2.3
S		0.2
O ^a		37.7
Component analysis (dried weight)		(wt%)
Cellulose		45.3
Hemicellulose		22.9
Lignin		31.1
Extractives		0.7

^a. Calculated from difference.

Red mud is a by-product of Aluminum company which contains high amount of iron oxides. FCC, ZSM-5, and red mud were tested as catalysts. Catalysts were calcinated at 550°C prior to each run. Red mud was activated according to procedure reported by Pratt and Christoverson.²⁰ BET and micropore surface area of catalysts were determined by N₂ adsorption measurement by Gemini V Series Surface Area Analyzers. Metal content of catalysts were analyzed by XRF analyzer (SPECTRO IQ II). Table 2 represents composition and some properties of catalysts.

2.2. Method

Table 2. Properties of catalysts

Catalyst	BET, m ² g ⁻¹	Micropore surface area, m ² g ⁻¹	Bulk density, g cm ⁻³	Main metal content
ZSM-5	355	237	0.34	SiO ₂ /Al ₂ O ₃ : 24
FCC	207	163	0.84	SiO ₂ /Al ₂ O ₃ : 0.68 Fe ₂ O ₃ :41.10%,
Red mud	158	n.d.	0.69	Al ₂ O ₃ :21.32%, SiO ₂ :17.02%

n.d.: not determined.

Pyrolysis experiments were carried out at two different heating rates; namely fast and slow in presence of catalyst. Analytical pyrolysis (Py-GC/MS) was performed using a CDS 2000 pyroprobe and a CDS AS-2500 autosampler (Chemical Data Systems, US). In a typical thermal pyrolysis, 10 mg of biomass sample was loaded into a quartz tube. In case of catalytic pyrolysis, biomass sample was placed between two catalyst layer with a ratio of 1:2:1 (catalyst: biomass: catalyst). The quartz tube was then placed to the probe, which is heated by a filament. Probe was heated to 500°C at a heating rate of 25°C min⁻¹ for slow pyrolysis and 1200°C min⁻¹ held at 500°C for 15 s. Sequential pyrolysis was also conducted with a fast heating rate (1200°C min⁻¹) at the various temperature intervals, i.e. 25°C-200°C, 200°C-300°C, 300°C-400°C, and 400°C-500°C. Sequential pyrolysis is denoted as S200, S300, S400 and S500, where numbers of labels show the final pyrolysis temperatures of each fragment.

A Perkin–Elmer AutoSystem XL Gas Chromatograph fitted with a DB 1701 column (60 m - 25 mm with 0.25 µm film thickness) was used to separate vapours produced with a split ratio of 1:25. The oven program was held temperature at 45°C for 4 min then heated to 240 °C at a rate of 4°C min⁻¹. The injector and detector temperatures were set at 28°C. Electron impact mass spectra were obtained by Perkin–Elmer MS GOLD (UK) at 70 eV. Proposed assignments of the main peaks were made from mass spectra detection using (NIST98 MS library). Identification of Py-GC/MS spectra was carried out by the comparison of the mass ions (m/z) of each peak. Relative area of individual compounds was calculated by taking into the consideration the GC peak areas to semi-quantify these compounds detected. Compounds that had concentration higher than 0.3% took into account for the calculation of relative area. The detected compounds were classified in terms of their chemical structures.

Thermal behaviour of olive pomace was also investigated in a thermogravimetric analyser (Elmer Diamond TG/DTA) under N₂ gas with a flow rate of 100 ml min⁻¹. Different heating rates (5°C min⁻¹, 10°C min⁻¹, 25°C min⁻¹, 50°C min⁻¹ and 75°C min⁻¹) were applied. Approximately 10 mg of olive pomace was placed in a ceramic crucible and heated from room temperature up to 900°C. Iso-conversional models, namely Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) were applied to determine apparent activation energy of olive pomace pyrolysis. KAS and FWO methods can be expressed by Equations (1) and (2), respectively.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE_a}{Rg(\alpha)}\right] - \frac{E_a}{RT} \quad (1)$$

$$\log(\beta) = \log\left[\frac{AE_a}{Rg(\alpha)}\right] - 2.315 - 0.457\frac{E_a}{RT} \quad (2)$$

where, β is the heating rate (K s⁻¹). A is the pre-exponential factor (s⁻¹), E_a is the apparent activation energy (kJ mole⁻¹). R is the gas constant (8.314 J mole⁻¹.K⁻¹). T is the reaction temperature (K) and $g(\alpha)$ is the temperature-independent function of reaction model. The conversion degree (α) is described in Eq. (3).

$$\alpha = \frac{(m_i - m_t)}{(m_i - m_f)} \quad (3)$$

where, m_i and m_f are the initial and final mass of olive pomace. m_t is the mass of olive pomace at time t . As the validity of iso-conversional method is limited according to conversion range, the values of E_a were determined in the conversion range of 0.1 and 0.8 for both models. E_a values were determined by plotting $\ln(\beta/T^2)$ against $1/T$ for KAS, while they were determined from linear plot of $\log(\beta)$ versus $1/T$ for OFW.

3. RESULTS AND DISCUSSION

3.1. Kinetic studies of olive pomace

The KAS and OFW plots of different conversion values (α) are presented in Figure 1. The coefficient of determination (R^2) values were higher than 0.95 for all cases, which is the evident of good fitting of model. In both methods, apparent activation energy increased at higher conversion degrees and temperatures. Yet, activation energy is not linearly dependent on the conversion. Lignin in biomass may be responsible for higher activation energy at higher conversion values. At higher temperatures, condensation reactions of the aromatic structure in lignin can occur, causing an increase in E_a .⁵ E_a values of OFW and KAS were quite similar for all conversion values. The mean values of E_a were found to be 105.6 kJ mole⁻¹ for KAS and 110.2 kJ

mole⁻¹ for OFW (see Table 3). Calculated E_a values in this study were close and lower than that in previous studies.¹⁶ Mishra and Mohanty¹⁶ reported that activation energies of different biomasses such as pine sawdust, poplar wood, rice husk and olive cake were between 127.8-350.2 kJ mole⁻¹ for KAS and 103.2-342.1 kJ mole⁻¹ for OFW model depending on the biomass type and heating rate.

Table 3. Activation energies at different conversion degrees

	KAS	R ²	OFW	R ²
Conversion (α)				
0.1	75.0	0.9556	80.0	0.9648
0.2	78.1	0.9704	83.6	0.9769
0.3	86.7	0.9691	91.9	0.9754
0.4	99.6	0.9740	104.5	0.9789
0.5	113.2	0.9779	117.7	0.9817
0.6	123.4	0.9839	127.5	0.9865
0.7	129.7	0.9824	133.7	0.9851
0.8	138.8	0.9874	142.6	0.9893
Mean	105.6		110.2	

3.2. Sequential pyrolysis

Sequential pyrolysis results for olive pomace are shown in Figure 2. The total amount of compounds detected was above 79% of total compounds. Notable differences on compounds can be seen in the first stage, which is a fraction of decomposed products up to 200°C. S-200 was found to have highest organic acids, namely acetic acid and heteroatom containing compounds. High acetic acid yield is in agreement with previous study conducted by Martinez and co-workers.²¹ Acetyl groups in hemicellulose started to eliminate at lower temperatures, which yielded acetic acid.

Phenolic compounds, mainly 2,6-dimethoxy-phenol, 2-methoxy-4-vinyl-phenol and 2-methoxy-phenol, started to form at further stages due to lignin decomposition at elevated temperatures. At lower temperature, ketone formation was lower than that of further steps. In the same manner, furans mainly occurred above 300°C. Levoglucosan was mainly formed at the first stage. Interestingly, levoglucosan could still observe above 300°C without decomposition. It should be also noted that bio-oil from second stage (S-300) had the highest furfural formation (2.97 %).

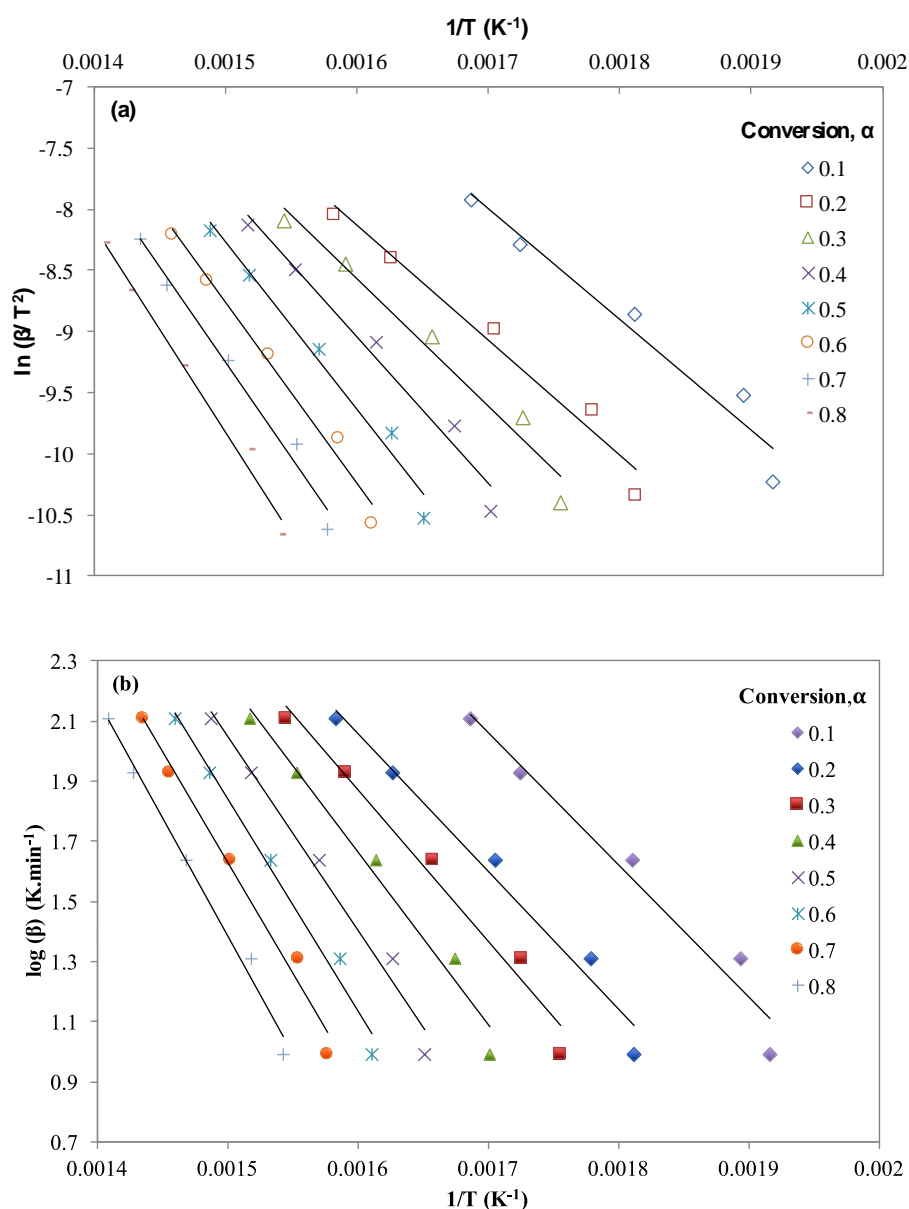


Figure 1. a) The plots of $\ln(\beta T^2)$ against $1/T$ for KAS method, b) The plots of $\log(\beta T^2)$ against $1/T$ for OFW method.

In a previous study done by Greenhalf and co-workers,²² sequential pyrolysis of willow SR was conducted at fast ($1500^\circ\text{C}/\text{min}$) and slow ($25^\circ\text{C}/\text{min}$) heating rates. They proposed that levoglucosan was converted into furfural at high heating rate, where as 2-furan methanol was obtained at lower heating rate. Based on these results, it is possible to obtain selective liquid products by sequential pyrolysis which makes the bio-oil more feasible for biorefinery purposes.

3.3. Effect of heating rate on pyrolysis products

Thermal experiments were performed in order to investigate the heating rates on bio-oil composition (Figure 3).

From Figure 3, some differences were found in the bio-oil compositions. For both heating rates, phenolic compounds are the main compounds in bio-oil. The amount of phenolics in bio-oil from fast pyrolysis was less than that from slow pyrolysis. This result is probably due to the fact that longer reaction time led to polymerization of phenolic compounds and formation of high molecular weight multi-ring structures which cannot be detected in GC-MS.²³

Fast pyrolysis produced more organic acids, particularly acetic acid and phenols whereas bio-oil from slow pyrolysis had more furans and aliphatic ketones, aldehydes and esters.

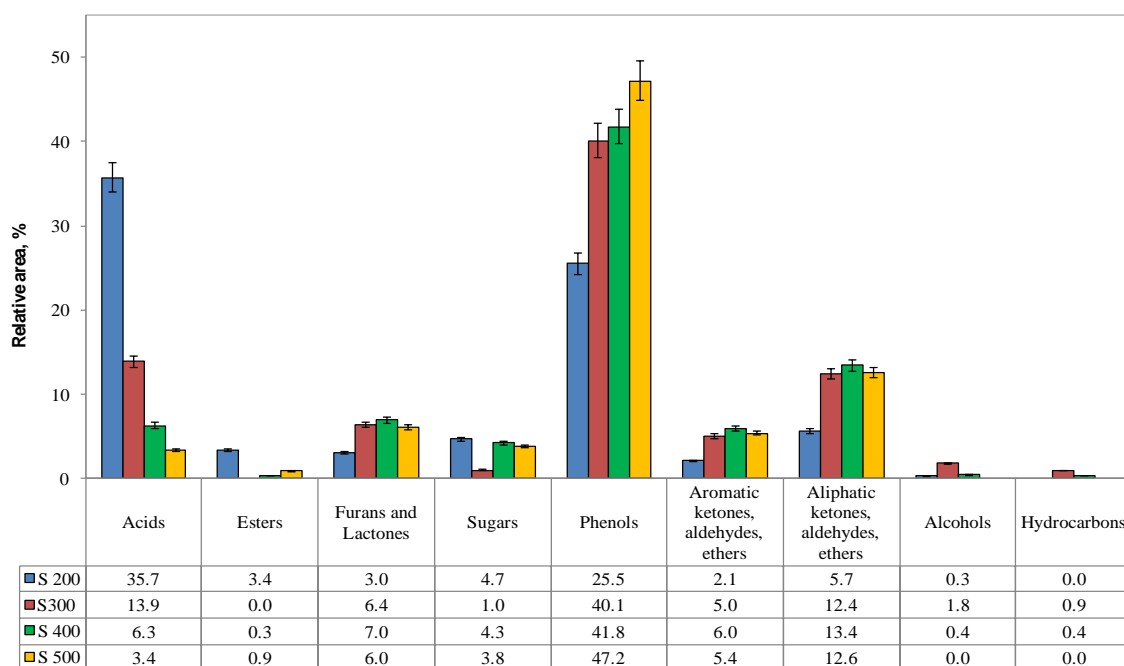


Figure 2. Relative peak areas of the products obtained from sequential pyrolysis.

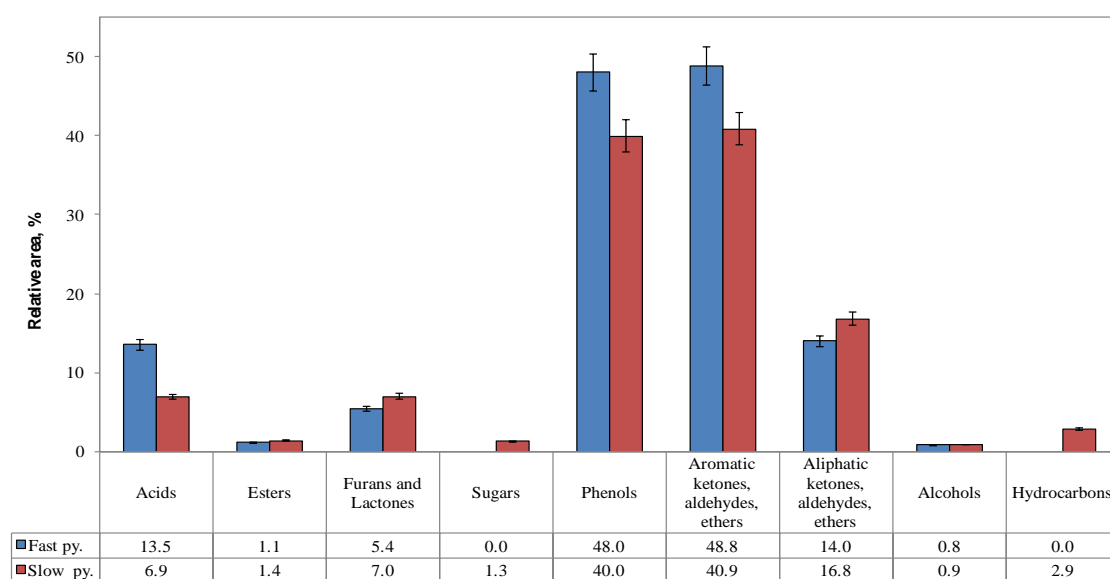


Figure 3. Relative peak areas of the products obtained by slow and fast pyrolysis.

Contrary to our results, Saftari and co-workers,²³ who investigated the effect of heating rate and temperature on products of pyrolysis of six different biomass, reported that high heating rate led to decrease in alcohol, ketone and aldehyde content, resulting from secondary reactions. It should be noted that long reaction times with slow heating rate may endorse secondary reactions, leading to convert organic acids to

other organic compounds. In addition, no hydrocarbons was obtained in fast pyrolysis whereas a small amount of hydrocarbons were detected in bio-oil from slow pyrolysis.

It was also noticed that distribution of individual furanic compounds varies at different heating rates (Table 3). The quantities of each individual compounds

were partially higher in case of slow heating rate. However, only the amount of furfural was slightly higher at fast heating rate. This result was consistent with possible mechanism of levoglucosan decomposition proposed by Greenhalf and co-workers.²² It was stated that the short residence times prevented the proton addition, resulting in the formation of furfural.

Table 3. Furanic compounds at different heating rates, relative area %.

	Fast Pyrolysis	Slow pyrolysis
Furan, 2-methyl-	-	0.5
Furfural	2.8	2.3
2(3H)-furanone, 5-methyl	-	0.32
Ethanone, 1-(2-furanyl)-	0.4	0.5
2-furan methanol	0.6	0.9
2-furancarboxaldehyde, 5-methyl-	-	0.3
2(5H)-furanone	0.8	1.0
Benzofuran, 2,3-dihydro-	0.5	0.6
Benzofuran, 6-methoxy-3-methyl-	0.3	0.5
Total	5.4	6.92

3.4. The effect of catalyst

Three different catalysts were studied in order to investigate the effect on pyrolysis product distribution in case of slow and fast heating rate (Figure 4).

In case of fast pyrolysis, all catalysts except for RM did not significantly effect on products. In presence of RM, phenolic compounds were decomposed while the relative amount of acids, furans and aliphatic ketones/aldehydes/ethers increased.

Differently from fast pyrolysis, bio-oil content varied depending on the catalyst in case of slow pyrolysis. Acidic compounds were increased in presence of all catalysts. Phenolic compounds were dramatically decreased in presence of RM and ZSM-5 whereas higher amount of phenolics were detected in bio-oil obtained in presence of FCC. It is known that ZSM-5 catalyst provides aromatization resulting from decomposition of phenolic composition.²⁴ However, none of aromatic compounds was detected in all pyrolysis products. This may be due to polymerization of aromatic compounds into high molecular weight compounds such as PAH and secondary coke formation onto catalyst surface.^{25,26}

On the other hand, the effect of RM on bio-oil

consumption is significant for both heating rate. The amount of phenols and aromatic ketones/aldehydes/ethers dramatically dropped by using RM, particularly in slow pyrolysis. This decrease can be attributed to formation of PAH compounds and coke formation in presence of RM as in case of ZSM-5. Similar results were found in previous studies reported by Veses and co-workers.²⁷ and Gupta and co-workers.²⁸ Gupta and co-workers²⁸ reported that relative yields of furfurals and organic acids increased and phenol yields decreased by using RM. They concluded that RM had furfural selectivity and facilitated the cleavage of carbon-carbon and carbon-oxygen bond in C6 and C5 molecules. In addition, high yield of acetic acid, which is product of hemicellulose via deacetylation, was attributed to synergistic effect of individual metal oxides in RM, mainly Fe₂O₃, Al₂O₃ and TiO₂. On the other hand, Veses and co-workers²⁷ found that PAH content of bio-oil decreased in case of mineral based catalysts whilst RM led to form PAH compounds. Since a considerable amount of phenols were converted into PAH, the relative percentages of acids, furan and aliphatic ketones/aldehydes/ethers increased in bio-oil.

4. CONCLUSIONS

In this study, pyrolysis of olive pomace at different conditions was investigated by using Py-GC/MS and TGA techniques. E_a of olive pomace pyrolysis is close (105.6 kJ mole⁻¹ for KAS method and 110.2 for OFW) and lower than that of different types of biomasses. For all cases phenolic compounds is the major compound ranging from 15.9% to 49.3% depending on experimental conditions. It was found that enrichment of individual organic compounds was achieved by conducting pyrolysis at different temperature intervals. Sequential pyrolysis seems a promising method to separate pyrolysis products, such as production of organic acids and alcohols at the low temperature stages, ketones/aldehydes and phenols at the high temperatures.

In case of catalytic pyrolysis, the effect of catalyst was more pronounced in case of slow heating rate due to high longer contact time between catalyst and pyrolysis vapor. Slow pyrolysis secondary reactions may take place at slow heating rates, resulting in formation of high molecular weight compounds via depolymerization. RM had the most effective catalyst on formation of acetic acid and furans while it decomposed phenolic compounds by reducing the yield from 48.0% to 36.6% and 40% to 15% in case of fast and slow pyrolysis, respectively. This study therefore exhibits a promising approach to produce targeted chemical compounds by selecting specific conditions for pyrolysis process.

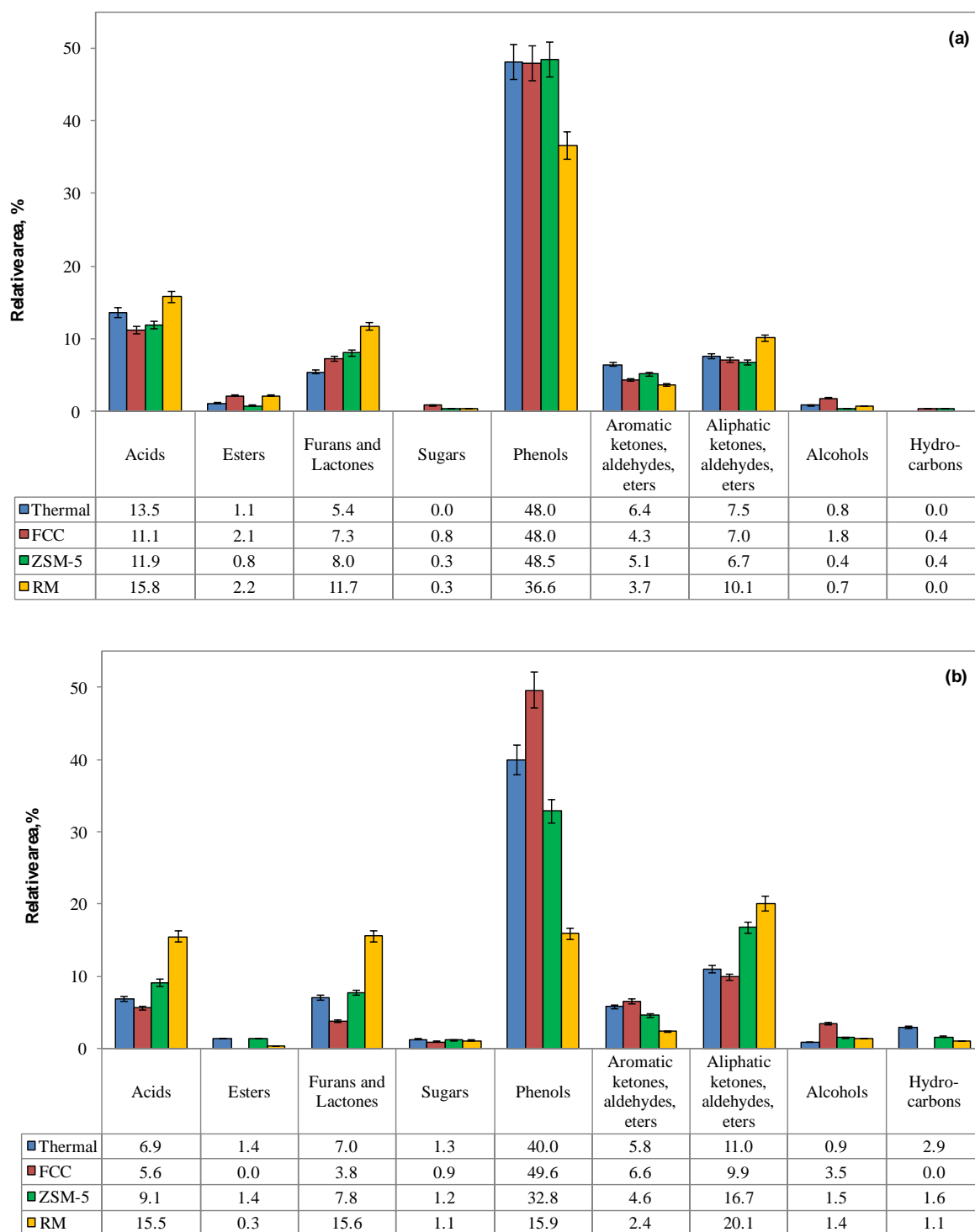


Figure 4. Effect of catalyst on bio-oil composition under a) fast heating rate, b) slow heating rate.

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Conflict of interests

I declare that there is no a conflict of interest with any person, institute, company, etc.

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