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Self-catalyzing pyrolysis of olive pomace

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ABSTRACT

In thisstudy, catalytic effect of intrinsic inorganics was evaluated by comparing pyrolysis end products obtained from pyrolysis of olive pomace (OP) in three different initial weights (30,100 and 200 g). Pyrolysis of OP with higher weights led to self-catalyzing pyrolysis resulting in approximately 20% bio-oil quantity increment when pyrolyzed OP weight increased from 30 g to 200 g. Additionally, both intrinsic inorganic percentages remained in pyrolysis chars and organic compounds in pyrolysis liquids altered with pyrolyzed OP weights. While the lowest inorganic percentage in chars was found at the pyrolysis of the highest OP weight, the highest belonged to 30 g OP pyrolysis. Moreover, while oxygenated compounds, namely aldehydes and ketones, in pyrolysis bio-oil decreased explicitly at 200 g OP pyrolysis, variety in alkane and alkene compounds enhanced at higher weights OP pyrolysis. Finally, the effects of temperature, heating rate and retention time on pyrolysis products were evaluated. Results showed that liquid products increased at 5 °C/min heating rate and decreased at 1 °C/min heating rate as pyrolysis temperature increased from 450 to 600 °C in the pyrolysis without retention time. However, reverse tendency was observed in liquid product quantities in the case of pyrolysis with retention time. Furthermore, while effect of temperature increment on pyrolysis gas and liquid was mostly opposite to each other in all pyrolysis conditions, bio-chars' quantity irregularly altered as to pyrolysis conditions.

1. Introduction

Thermochemical conversion of biomass is one of the effective ways to convert high quantities of biomasses to useful products which can be used for diverse purposes such as energy supply or product recovery. Among these biomasses, agricultural wastes, like olive pomace (OP), are the commonly used waste types based upon their characteristics and high quantities [1,2].

OP is the solid waste of olive oil production process and consists of water, pulp, oil, olive skin and olive pits. Although its ingredients change based on the source of olive, environmental issues, time of storage and extraction methods used in the olive oil production [3], it mainly includes polysaccharides, proteins, other pigments, ligno-cellulosic polyalcohols, polyphenols, fatty acids and various inorganic components [4,5]. Pyrolysis is a commonly used thermochemical process for OP, since produced end products in OP pyrolysis can be utilized in various forms. For example, pyrolysis gas and liquid products can be used as fuel, pyrolysis char can be used in adsorbent production or for soil amendment [6].

There are several factors which affect pyrolysis kinetics and mechanism such as pyrolysis conditions (temperature and heating rate) and retention time. When pyrolysis is conducted at high heating rate and temperature, yield of gas product is enhanced compared to liquid and solid end products. Hmid et al. obtained higher pyrolysis char quantities at 25 °C/min heating rate compared to 45 °C/min and temperature increment of 10 °C resulted in pyrolysis chars decrement in OP pyrolysis [7]. Similarly, higher gas yield was observed at higher heating rate and temperature in another OP pyrolysis study [8]. As for retention time and catalyst effect on pyrolysis process, their effects on pyrolysis product can be stated as variable. In a majority, short retention time results in higher liquid end product due to inhibition of secondary reactions led to gas production [6]. However, retention time effect on gas and solid end products of pyrolysis can be variable. As retention time increased increment was found in char and gas product proportion in the cotton gin trash pyrolysis study [9], whereas, no net effect of retention time on gas product was observed in crop residue mixture pyrolysis [10]. Although some studies about retention time effect on biomass pyrolysis exist, no study found for fully description of retention time effect on OP pyrolysis. Similar to retention time, catalysts effect on OP pyrolysis can differ based on some factors like catalysts types. In OP pyrolysis, some catalysts have been used widely. While some, such as dolomite, red mud, chars of brown coal and OP, Fe or Ni based brown coal and OP, MgO and MgO (5% Co), catalysts cause reduction in the liquid and increment in gas end products [8,11–13], some of them, like

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$ZnCl_2$, have a reverse situation [14]. MgO catalyst resulted in a considerable increment in gas quantities, especially in CO_2 yield of 15.7 wt.%, due to ketonisation and aldol condensation reactions [13]. $ZnCl_2$ led to increase hydrogen rich gaseous quantities however, total quantities of pyrolysis gas decreased with $ZnCl_2$ catalyst [14]. In addition to these catalysts, there are also some catalysts used in OP pyrolysis which have irregular effects on pyrolysis products: K_2CO_3 and Na_2CO_3. These two catalysts weaken C—C bond due to transfer mechanism of oxygen and prevent stable chemical structure generation by alkalis in catalyst structure thereby, they provide decrement in activation energy for complex pyrolysis reaction [14]. Moreover, in another study about alkali catalyst, it was stated that when catalyst has alkali metals, char catalytic activity increases since they easily undergo gasification reaction [12]. All these findings about catalytic pyrolysis of biomass have started to prompt researchers to investigate catalytic effect of intrinsic inorganics of biomasses during pyrolysis and evidences about catalytic effect of inorganic components, such as K, P, Ca, Mg, Fe, Na etc., naturally found in the biomasses [15,16]. However, most of these studies based only on some ligno-cellulosic biomasses, especially woody biomass, and studies about catalytic effect of intrinsic inorganics during pyrolysis process has been performed by using thermogravimetric analysers (TGA). For instance, By comparing TGA and/or DTG findings, Carvalho et al. observed that K has catalytic effect on both gasification and pyrolysis process of pinewood, whereas, catalytic effect of Ca is lower in pyrolysis and higher in gasification process [16]. The authors also emphasized that releasing volatiles and char oxidation stages are catalyzed with K by shifting DTG characteristic peaks of these stages to lower temperatures [16]. In another study about catalytic effect of intrinsic inorganics in pine wood pyrolysis, it was observed that the effects of K on pyrolysis process are much higher as compared to other inorganics; especially first order activation energy decrease by 50 KJ/mol when K ions are used [15]. Nanou et al. revealed that woods having different inorganic composition showed different thermochemical behavior during gasification process [17]. There is a significant gap in the literature about changes in inorganic content of pyrolysis chars and pyrolysis liquids organic fractions due to the catalytic effect of intrinsic inorganics [12–17]. Nonetheless, investigation of inorganics remaining in pyrolysis chars can be stated as one of the critical points during catalytic pyrolysis since inorganics can also be transformed into organic forms, which affects pyrolysis liquids contents and quality [18].

By far, although various catalytic effects of inorganic components on OP pyrolysis has been investigated, intrinsic inorganics in OP effects on pyrolysis products have not been studied in detail yet. However, inorganics, which are indicated having catalytic effects during pyrolysis process such as K, Ca, Fe and Mg etc., already exist at high proportions in OP [19], therefore, effects of intrinsic inorganics should be evaluated. Moreover, although heating rate and temperature effect on OP pyrolysis end products has been evaluated by many researchers, retention time and effects of different pyrolysis conditions combinations on especially inorganic components in OP pyrolysis chars and liquids can be stated as deficiencies in studies. In this regard, in this study, the catalytic effects of intrinsic inorganics in OP on pyrolysis was revealed by comparing OP pyrolysis having different initial weights and so, different intrinsic inorganic quantities. Within this scope, catalytic effect of intrinsic inorganics was evaluated based on pyrolysis product yields, inorganic contents of pyrolysis chars as well as organic fractions of pyrolysis liquids. Moreover, different temperature, heating rate and retention time effects during OP pyrolysis were revealed simultaneously. Additionally, effects of retention time at different temperatures and heating rates in OP pyrolysis was investigated.

2. Material and method

Two phase wet OP was obtained from an olive mill in Mersin (Turkey) and characteristics of wet OP sample was determined. Within the scope of the study, catalytic effects of intrinsic inorganics were revealed by pyrolysis of different OP weights at the same pyrolysis conditions. Additionally, temperature, heating rate and retention time effects on pyrolysis end products of OP with the same weight were investigated. Initially, 30,100 and 200 g wet OP samples were pyrolyzed in fixed bed batch pyrolysis system at 400 °C with 1 °C/min heating rate in order to investigate the catalytic effect of intrinsic inorganic components in pomace on pyrolysis end products yield and pyrolysis bio-oil components. Secondly, 100 g OP was pyrolyzed at three different temperatures, 450 °C 500 °C and 600 °C, at 1 and 5 °C/min heating rates with/without 30 min waiting after reaching the pyrolysis temperature to observe retention time and heating rate effect. At the end of the pyrolysis processes, pyrolysis oil and chars were collected separately, gaseous end products were collected at gasometer system. Pyrolysis char and liquid end products at the end of the pyrolysis were weighed with Mettler Toledo ME204 laboratory balance and measured weights were expressed as percentage (w/w%). Remaining percentage was evaluated as pyrolysis gas proportion.

Pyrolysis chars and raw OP sample were analyzed at ICP-OES after microwave pretreatment to determine inorganic components simultaneously in a sample. Microwave pretreatment process was conducted at 200 °C temperature after addition of 5 mL concentrated nitric acid, 3 mL concentrated hydrochloric acid and 2 mL distilled water on 0.2 g pyrolysis char.

GC–MS was used to evaluate changes in organic fractions of OP pyrolysis liquids. AOC-20i liquid extraction method by dichloromethane was applied before GC–MS analysis for extraction of organic compounds in OP pyrolysis liquids. In GC analyses, 30 m × 0.25 μm × 0.25 μm (L × D × T) DB-5MS capillary column was used and carrying gas (helium) flowrate was arranged as 1.2 mL/min. Injection volume of extracted sample and injection temperature was selected as 1 μL and 250 °C respectively. GC oven was run at programmed temperature as follows: Initial oven temperature was 40 °C, temperature was increased to 300 °C within 32.5 min and hold at 300 °C for 12.5 min.

3. Results and discussion

3.1. Raw OP inorganic content

Inorganic contents of raw OP were specified simultaneously with ICP-OES after microwave pretreatment process and catalytic effect of these inorganics to OP pyrolysis process was evaluated since it is known that even though low quantities of these inorganic compounds have catalytic effect on thermal degradation process of lignocellulosic biomass. Existence of these inorganic components highly affect pyrolysis products yields and composition [20]. Major inorganics in OP content were K, P, Ca, Mg, Fe, while minor ones were B, Ag, Cr, Mn and Ni (Table 1).

There are some researches showing that inorganics have an important effect during OP pyrolysis. In a study conducted by Duman

Table 1
Raw OP inorganic components.

Inorganics	Quantities (mg/g)
K	12.32
Ca	3.85
P	1.02
Mg	0.96
Fe	0.24
Na	0.16
B	0.02
Mn	0.01
Cr	0.003
Ag	0.002
Ni	0.001
Total	18.58

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