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Tailoring Cu/Al_2O_3 catalysts for the catalytic pyrolysis of tomato waste

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ABSTRACT

In this study, pyrolysis of tomato waste has been performed in fixed bed tubular reactor at 500 °C, both in absence and presence of Cu/Al_2O_3 catalyst. The influences of heating rate, catalyst preparation method and catalyst loading on bio-oil yields and properties were examined. According to pyrolysis experiments, the highest bio-oil yield was obtained as 30.31% with a heating rate of 100 °C/min, 5% Cu/Al_2O_3 catalyst loading ratio and co-precipitation method. Results showed that the catalysts have strong positive effect on bio-oil yields. Bio-oil quality obtained from fast catalytic pyrolysis was more favorable than that obtained from non-catalytic and slow catalytic pyrolysis.

1. Introduction

The world has faced an energy crisis caused by the increasing demand for fossil fuels and corresponding price rises [1]. Among renewable energies, biomass is one of the most plentiful and well utilized sources in the world. So, biomass can be considered as the only sustainable alternative to fossil fuels talented of yielding petroleum like products [2,3]. Obtaining energy from biomass can be achieved by biochemical and thermochemical processes. Pyrolysis process seems to be one of the promising methods for converting biomass to fuels via thermo-chemical decomposition of organic materials at elevated temperatures without oxygen [4,5].

The direct use of liquid product obtained from pyrolysis is very difficult for transportation fuels because of its complex composition such as acids, aldehydes, ketones, unsaturated compounds. Due to reactive oxygen compounds, bio-oil is unstable under the conditions of higher water content and an increase in viscosity over time. Additionally, petroleum oil's energy content is much higher than that of bio-oils because of high water (15–30 wt.%) and oxygen contents (40–50 wt.%) [6].

Currently, there are several techniques to attain the removal of oxygen, including catalytic pyrolysis and cracking, hydrogenation, hydrodeoxygenation, steam reforming, molecular distillation, supercritical fluids, esterification and emulsification. Hydrogenation is the most effective method to remove oxygen compounds so far; however it requires to work with hydrogen at high pressures (30–140 bar). On the other hand, catalytic pyrolysis has gained an admirable interest due to the benefits of operating at atmospheric pressure for both safety and economic reasons [7,8].

In catalytic pyrolysis, the catalysts facilitate the reaction of cracking of carbon–carbon bonds and also enhancing de-oxygenation in which obtained bio-oil is lower in oxygenates, has a higher calorific value and better hydrocarbon distribution. Therefore fuel quality of catalytic pyrolysis bio-oil is better than conventional pyrolysis oil [9]. Depending upon the method of contacting catalyst and pyrolysis vapors, the process may be divided in different groups: In the first group, the catalyst is directly mixed with the biomass to be pyrolyzed (in-situ). In the second group, biomass is separately pyrolyzed and the resulting vapor products are transported to a catalysts bed downstream of the pyrolyzer (ex-situ) [10].

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By-products of fruits and vegetables processing represent a critical disposal problem for the industry concerned, however they are favorable sources of compounds which may be used for various purposes in the food, pharmaceutical and cosmetic industries [11]. In this study tomato processing industries' wastes are selected as raw materials. Tomato (*Solanum lycopersicum*) is, after potato, the second most consumed vegetable in the world and approximately 30% is consumed as processed products. Besides, tomato is one of the most common vegetables in Turkey and quiverful of solid wastes are produced by the tomato processing industry [11–13]. About 10–40% of the total tomato processed in a plant is as skins and seeds, which are usually used for animal feed.

Agricultural wastes and tomato plant's wastes, peels and seeds are getting more attention in recent years. Mangut et al. reported about characterization of the biomass residue from tomato processing industry by paying special attention to the kinetic of pyrolysis [14]. The experimental technique used in their study was the thermogravimetric analysis (TGA). They found out that peels, seeds and peels and seeds biomass residues from tomato processing industry have a low S, and ash contents and a high volatile content and HHV, which could make them an interesting source for thermal energy production. The kinetic model assumes that the kinetic of the thermal decomposition of these biomass materials can be simulated by independent reactions associated with the thermal decomposition of some fractions of hemicellulose, cellulose, lignin and oil. Font et al. also studied about kinetics and thermal decomposition of tomato plant under different conditions by TG and TG–MS [15]. According to their experiments and calculations, two kinetic models for the pyrolysis and combustion of tomato plant have been obtained, which correlate dynamic and isothermal runs with the same set of parameters. Hossain et al. presented agronomic values of a biochar produced from wastewater sludge through pyrolysis at a temperature of 550 °C [16]. Application of biochar was also found to significantly increase the soil electrical conductivity as well as phosphorus and nitrogen contents. Celma et al. generated large volumes of residual biomass (mainly peels and seeds) from tomato industrial processing plants [17]. The analysis of some physical–chemical properties of pellets manufactured from industrial tomato residues (peels and seeds), particle and bulk densities, hardness and durability was reported. The highest values for durability (91.2%) and hardness (88 N) were observed for pellets set as 9.09 wt% w.b. final moisture content. Sabio et al. investigated the influences of the temperature, residence time, and biomass/water ratio variables on the hydrothermal carbonization (HTC) of tomato peel [18]. A Central Composite Design method was implemented to define the number and the conditions of the experiments to perform. The resulting experimental data were fitted by a 2nd-order model, allowing the behavior of the process to be simulated with accuracy.

In recent years, various catalysts were used for pyrolysis process such as zeolites, aluminum oxide, Al-MCM-41, CaO and MgO. Inaba et al. reported that H-ZSM-5 and H-Beta showed high activity for the formation of non-oxygenated aromatic products. When H-ZSM-5 was used, higher Si/Al_2 ratio led to decrease in yield of non-oxygenated aromatics. When H-Beta was added, even high Si/Al_2 ratio led to high yield of non-oxygenated aromatics [19]. Liu et al. used γ-Al_2O_3 for catalytic pyrolysis of Chlorella to obtained obtain high-quality bio-oil [20]. The effect of Cu/Fe/Zn containing Al-MCM-41 type catalysts on bio-fuels and chemicals production was investigated by Antonakou et al. They found that all catalysts increased the amount of phenolic compounds [21]. Wang et al. used the MCM-41 and CaO catalysts for catalytic pyrolysis of biomass. CaO catalyst was very effective in deacidification and the formation of hydrocarbons and CH_4 was promoted by the conversion of acids [22]. Pütün investigated the effect of various amounts of MgO catalysts on cotton seed pyrolysis. He found that the bio-oil quantity was decreased by catalyst addition, although the bio-oil quality in terms of hydrocarbon distribution, calorific value, and elimination of oxygenated groups was increased [23].

Sun et al. employed Fe/ZSM-5 catalyst for fast pyrolysis of biomass to aromatics [24]. By the catalytic pyrolysis of biomass at 600 °C the aromatics were produced in the greatest amounts. The introduction of Fe on ZSM-5 improved the yields of monoaromatic hydrocarbons.

Sun et al. also reported that they prepared Fe/CaO catalysts with different Fe contents (5–15 %wt.) and used them for fast pyrolysis of sawdust by Py-GC/MS experiments [25]. They found that the catalytic activities in upgrading bio-oils were inhibited with the increase of Fe contents. Besides, the %5 Fe/CaO catalyst displayed the best performances among the three catalysts. The same group also reported Fe/CaO catalysts were prepared by impregnation and mechanical mixing methods and the effects of preparation methods on the pyrolytic products were studied [26]. The im-Fe/CaO catalyst displayed better performances than the mix-Fe/CaO catalyst. According to the results, the higher activity is attributed to the stronger metal support interaction. Murata et al. investigated fast pyrolysis with cheap Ni-based catalysts to produce bio-oil from jatropha residues via Py-GC/MS [27]. Under the studied Py-GC/MS and stainless-steel reactor used pyrolysis conditions, Ni-based catalysts seems to be better and cheaper candidates than PtPd systems. Jiang and co-workers investigated pyrolysis of the large particle oil shale in a self-made retorting pyrolyzer in order to obtain the optimal final pyrolysis temperature of Huadian oil shale and evaluate the catalytic performance of transition metal salts ($CoCl_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$) in promoting the shale oil yield and product characteristic [28]. The experiment results showed that the use of $CoCl_2 \cdot 6H_2O$ salt further increased the oil yield. In addition, the addition of the Co salt significantly enhanced the formation of aromatic hydrocarbons in the shale oil, which increased about 18% compared to that of non-catalytic pyrolysis. Ma et al. reported that catalytic pyrolysis of flame retarded high impact polystyrene (Br–HIPS) using three zeolite materials (HY, Hβ and HZSM-5) and two mesoporous solids (all-silica MCM-41 and active Al_2O_3) [29]. The highest oil yield of 67.9 wt.% was obtained in the presence of all-silica MCM-41. HZSM-5 and all-silica MCM-41 produced more valuable single ring aromatics. The results confirmed the catalytic pyrolysis of Br–HIPS and debromination performance was well related to the textural properties of catalysts.

However, the pyrolysis of tomato industry waste has not sufficiently investigated by the limited numbers of works mentioned above. In the present study, non-catalytic and catalytic conversion of tomato industry waste biomass were studied with and without the use of a Cu/Al_2O_3 catalysts. Besides, there exits no study in the literature on the pyrolysis of the tomato waste used with metal oxide catalyst. Hence it was decided to study the effectiveness of metal oxide as a catalyst on the yield and quality of pyrolytic bio-oil. Additionally, no references have been found in literature concerning the pyrolysis of tomato waste. Due to a limited number of references in relation to pyrolysis of tomato waste, the contribution of this paper to the literature can be crutial. Therefore, in this study, considering it as one of the promising species for production of bio-oil, it has been performed the catalytic and non-catalytic pyrolysis at fixed temperature of 500 °C in nitrogen atmosphere (100 cm^3/min). Effects of pyrolysis parameters such as heating rate, catalyst preparation method and copper loading ratio were investigated. Furthermore, bio-oils obtained from pyrolysis have been characterized by elemental, gas chromatography–mass spectroscopy (GC–MS) and Fourier transform infrared spectroscopy (FT-IR) analysis.

2. Experimental

2.1. Biomass sample

Tomato waste was obtained from a food factory located in Bursa, western part of Turkey. Prior to use, air-dried tomato waste was ground in a cutting mill and sieved to give fractions of $D_p > 1.8$ mm, $1.8 > D_p > 0.85$ mm, $0.85 > D_p > 0.425$ mm, and $D_p > 0.425$ mm. Mean particle size was specified as 0.655 mm. Proximate analysis was applied on tomato waste sample to detect the weight fractions of volatile matter, ash, moisture and fixed carbon. The ultimate analysis was performed using an elemental analyzer (Leco CNH628 S628). The results of ultimate and proximate analyses of tomato waste were given in the previous study [30].

2.2. Preparation of catalysts

The catalysts used in this study were produced by two different compositions (5 and 10 wt.% Cu loading) and methods (sol–gel and co-precipitation). In sol–gel method, hydrate nitrates of the selected metals ($Al(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$) were used as precursors due to their higher solubility in water and homogeneity. The nitrates were further mixed with deionized water and citric acid in appropriate amounts. To adjust the pH of the solution around 6, 1 M $(NH_4)_2CO_3$ was added. Rotary evaporator was used to concentrate the resulting solution until a gel was obtained [31]. The gel was dried in an oven, ground, kept at 200 °C and then calcined at 700 °C for 5 h under static air with a heating rate of 5 °C/min 5 and 10 wt.% copper-loaded catalysts prepared by sol–gel method were designated as SG1 and SG2, respectively.

The catalysts were also prepared by the co-precipitation method. To synthesize co-precipitated catalysts, an aqueous solution containing $Al(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were simultaneously precipitated using 1 M KOH until reaching pH 10. The co-precipitated sample was washed, filtered and dried at 110 °C for 12 h in air, followed by calcination with the same conditions described in sol–gel method. 5 and 10 wt.% copper-loaded alumina catalysts prepared by co-precipitation method were assigned as CP1 and CP2, respectively [32].

2.3. Apparatus

The pyrolysis experiments were carried out under nitrogen atmosphere (100 cm^3/min) in a well-swept and fixed-bed tubular reactor with a length of 90 cm and an inner diameter of 2.5 cm made of 310 stainless steel. AC voltage was directly applied to heat the reactor; so there was no need to use any furnace. During the experiments, temperature and heating rate were measured with a PID (proportional-integral-derivative) controller. Temperature measurements were taken using thermocouple which was placed in the middle of the reactor. The experiments were performed at atmospheric pressure. A rotameter was used to control the nitrogen flow rate before entering the reactor.

2.4. Experimental procedure

Experiments were performed both in the absence and presence of Cu/Al_2O_3 catalyst. For the first group of the experiments, to determine the heating rate effect on thermal pyrolysis yields, 10 g of tomato waste was put into the reactor under 100 cm^3/min sweeping gas (N_2) velocity which was adjusted with a rotameter. The sample was heated up to a constant temperature of 500 °C with heating rates of 40 and 100 °C/min. After attaining the final pyrolysis temperature, the sample was held for 15 min.

In the second group of experiments, the aim was to investigate the effect of Cu/Al_2O_3 catalyst preparation method (sol–gel and co-precipitation) and catalyst loading ratio (5 and 10 wt.%) on product yields and quality. Generally, a biomass sample is physically mixed with catalyst and pyrolyzed at desired temperatures in “in situ” catalytic pyrolysis. In this work, 0.5 g catalyst was mixed with 9.5 g tomato waste at pyrolysis temperature of 500 °C with 100 cm^3/min sweeping gas (N_2) velocity and heating rates of 40 and 100 °C/min.

Four traps placed in an ice bath were used to condense volatile products to obtain liquid products. The aqueous layer in the liquid product was separated from the organic layer with a separatory funnel. The solvent was removed in a rotary evaporator at 40 °C, the bio-oil was obtained by weighing the remaining part. The residual solids in the reactor were weighed as char. The gas yield was calculated from the difference. All the yields were expressed on a dry and ash-free basis, and their values were taken as the average of at least three parallel experiments error less than ±0.5%. Pyrolysis product yields were based on mass percentage.

2.5. Characterization of catalysts and bio-oil

The X-ray diffraction method (XRD) was used to identify phase structure and determine the relative crystallinity of the catalysts. XRD measurements were carried out using CuKα radiation on a PANalytical X'Pert Pro Materials Research Diffractometer. The X-ray tube was operated at 45 kV and 40 mA and the X-ray pattern was scanned with a step size of 2°/min from 10 to 90° (2θ). The surface area of each catalyst was calculated from N_2 adsorption/desorption isotherms by using BET (Brunauer–Emmett–Teller) method with Micromeritics Asap2020 analyzer. SEM images of the catalysts were obtained by using Zeiss Supra VP40 Scanning Electron Microscope. Samples were placed on carbon bands and coated with a platinum thin layer in argon atmosphere using Quorum Q150RESDC Sputter Coater. Proximate and elemental analyses (Leco CNH628 S628) were performed on bio-oil samples. Elemental analysis was calculated on a dry ash-free basis. Additionally; higher heating values (HHV) of the bio-oils were calculated from elemental analyses data by Dulong's Formula [33]:

$$\text{HHV (MJ/kg)} = 33.83C + 144.3(H-O/8) + 9.42S \quad (1)$$

Gas chromatography/mass spectroscopy (GC/MS) analysis for bio-oils was performed using a QP2010 Model gas chromatograph and a mass selective detector (Shimadzu, Japan); a thin film (30 m × 0.25 mm, 0.25 μm film thickness) TRB-5 MS capillary column supplied from Teknoroma was used. Carrier gas was helium with a flow rate of 1 cm^3/min. The temperature program was 40 °C for 5 min followed by 4 °C/

min heating rate to 260 °C. The compounds were identified using NIST library. The FT-IR spectrum of bio-oil was recorded using a Perkin Elmer Spectrum 100 Model in wave number range of 4000–400 cm^{-1} by ATR module.

3. Results and discussion

3.1. Characterization of catalysts

The effects of catalyst preparation method and copper loading ratio on the crystal structure of the catalysts were investigated via XRD patterns. As shown in Fig. 1, crystalline peaks are identified as monoclinic CuO, orthorhombic CuO_2, cubic Cu_2O and cubic Al_2O_3. The formations of CuO_2 at 2θ values of 47° and 54°, and also Cu_2O at 31.5° seen in SG1, SG2 and CP1 are thermodynamically possible on Cu–Al contact surfaces. The CuO phase observed in only CP2 catalyst at 2θ values of 36.5° and 41.7° is due to the reduction of Cu via an intermediate phase of Cu_2O rather than undergoing a direct reduction to elemental copper. This also indicates that the spinel structures were formed because of well dispersed copper on the catalyst surface during the synthesis. Indeed, formation of $Cu_xAl_yO_z$ phase revealed at copper-alumina interface that causes strong bond at the interfaces [34].

The obtained Cu/Al_2O_3 powders from different synthesis methods and copper loading ratios were further comparatively examined in terms of their specific surface area. The surface areas of the catalysts were measured by means of conventional Brunauer, Emmett, and Teller (BET) method. Based on the different preparation methods, catalysts with different specific surface areas were obtained (Table 1). Textural characterization by N_2 adsorption/desorption isotherms shows that catalyst prepared by sol–gel method with 5% copper loading exhibits the largest surface area of 221.89 m^2/g among the synthesized catalysts. On the contrary, catalyst prepared by co-precipitation method with 10% copper loading has the lowest surface area. It is seen from Table 1 that the catalysts prepared by sol–gel method provided a larger available area than the catalysts prepared by co-precipitation method. An increase in metal loading generally causes a decrease in the surface area of the supported reagent consistent with the blocking of pores and surface irregularities.

The effects of catalyst preparation method and copper loading ratio on the catalyst morphologies and shape of the grains were evaluated by SEM analysis (Fig. 2). Fig. 2 shows that most particles have a rough surface morphology. All the catalyst powders contain small and big particles and also irregular shapes with a large agglomeration. Since particles have a non-uniform size distribution, it is not possible to identify particle sizes from SEM images directly. But it can be concluded that the agglomeration during sintering process results in larger particle sizes. The SEM images indicate fairly homogenous distribution of alumina in Cu matrix for all catalysts.

3.2. Pyrolysis yields

3.2.1. Effect of heating rate

In order to investigate the heating rate effect on pyrolysis yields, experiments without catalyst were performed at heating rates of 40 and 100 °C/min under nitrogen atmosphere (100 cm^3/min). The final temperature was 500 °C and holding time at this temperature was 15 min. From previous studies, it is known that the conventional slow pyrolysis enhances char formation, whereas fast pyrolysis is preferred when bio-oil is the target product [35–37]. This can be explained by the fact that the higher the heating rate, the less time is available for tar cracking and subsequently the less char and more tar were produced. In fact, higher heating rates reduced mass and heat transfer limitations which resulted in higher oil yields [38]. Fig. 3 shows the differences between fast and slow pyrolysis on product yields. Bio-oil yield is attained as 25.25% for slow pyrolysis (40 °C/min), and 26.68% for fast pyrolysis (100 °C/min). Higher heating rates favour gasification reactions, therefore bio-oil yield was found around 26% although the heating rate was increased from 40 to 100 °C/min. Heating rates of 40 and 100 °C/min are quite close to each other. According to this reason, similar bio-oil yields are not surprised. It can be seen from Fig. 3 that higher heating rate increased bio-oil yield up to 5.7% and had a positive effect on liquid product yield. Increasing the heating rate caused a decrease in char yield from 34.51 to 26.07% and an increase in gas yield from 29.19 to 35.92%.

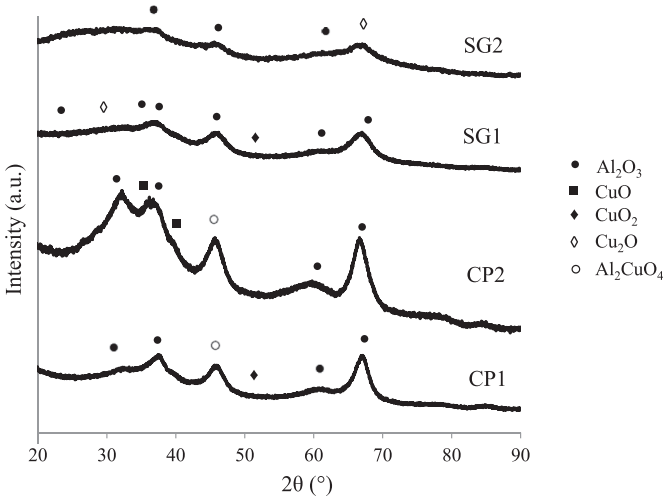

Fig. 1. XRD patterns of the Cu/Al_2O_3 catalysts.

Table 1
BET surface areas of the catalysts.

Catalyst Code	Specific surface area (m^2/g)
CP1	200.30
CP2	50.23
SG1	221.89
SG2	94.13

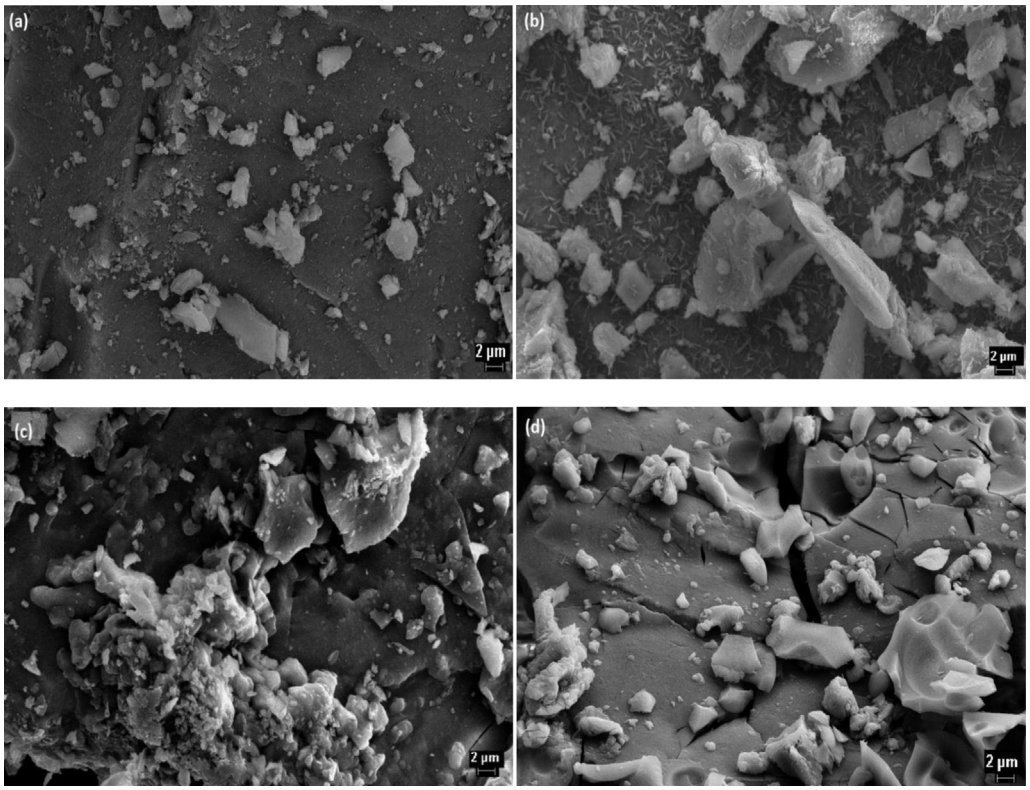

Fig. 2. Scanning electron micrographs of (a) CP1, (b) CP2, (c) SG1, and (d) SG2 catalysts at 5 Kx magnifications.

3.2.2. Effect of catalyst preparation method and copper loading ratio

Figs. 4 and 5 show the effects of catalyst preparation methods (sol–gel and co-precipitation) and catalyst loading ratios (5 and 10%) on the product yields for slow and fast pyrolysis experiments, respectively.

As seen from Fig. 4, catalyst preparation method slightly affects the product yields for slow pyrolysis. Higher bio-oil yields were obtained when co-precipitated catalysts were used. Higher activities of the co-precipitated catalysts are attributed to the stronger metal support interaction between Cu and Al_2O_3 support confirmed by formation of $Cu_xAl_yO_z$ phase. 5% Cu/Al_2O_3 catalyst prepared by co-precipitation method (assigned as CP1) produced the highest bio-oil yield of 25.18%. Increasing the metal loading ratio resulted in the reduction of

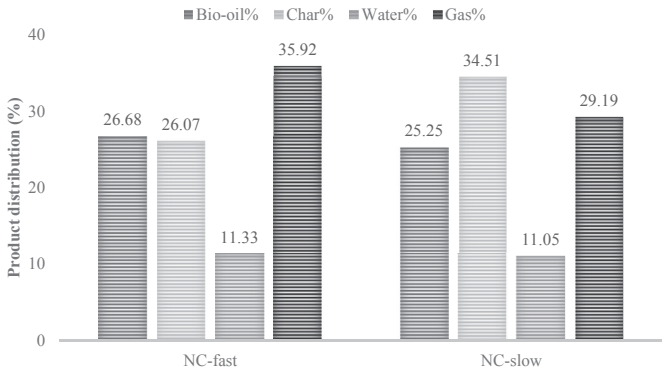

Fig. 3. Effect of heating rate on non-catalytic pyrolytic yield.

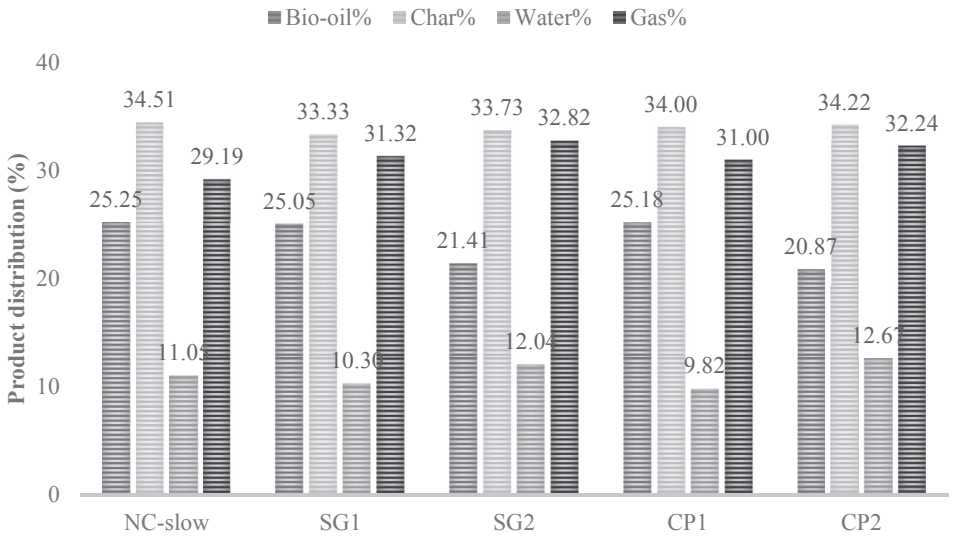

Fig. 4. Effect of catalyst on tomato waste pyrolytic yield at heating rate of 40 °C/min.

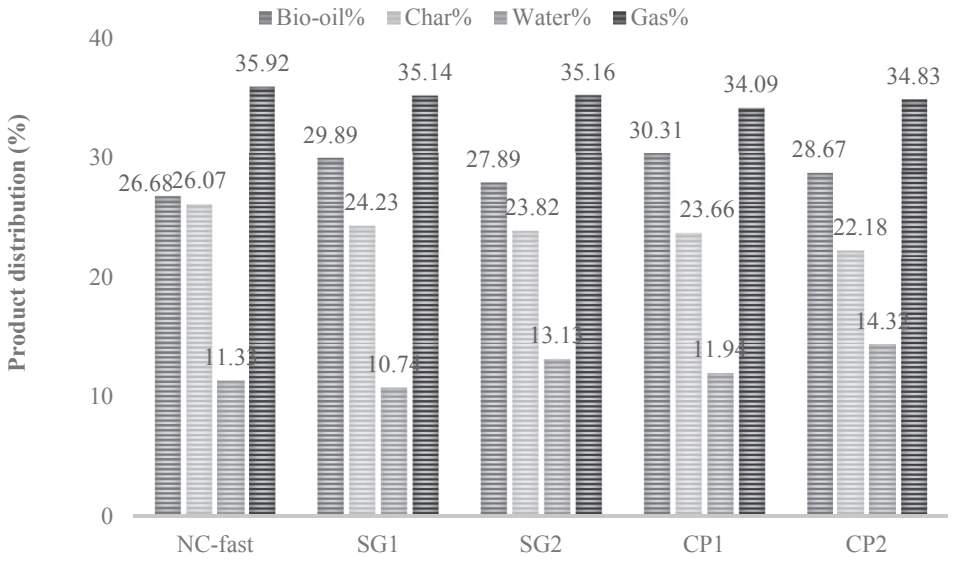

Fig. 5. Effect of catalyst on tomato waste pyrolytic yield at heating rate of 100 °C/min.

bio-oil yield. This can be related to the limited selectivity of the catalysts on conversion of bio-oil when more than 5% metal loading was added into the catalyst during the preparation. This limited selectivity can be based on the following reasons. Firstly, the agglomeration of the copper particles results in lower surface areas and active sites of metals, especially when copper loading is higher than 5%. This behavior is also confirmed by BET results (Table 1). Secondly, the activation energy for pyrolytic reactions increases with the additional copper loading [39].

Fast pyrolysis results are given in Fig. 5. The bio-oil yield, which was obtained as 26.68% without catalyst, reached the maximum value of 30.31% by using 5% copper loaded co-precipitated catalyst. Comparing the catalyst preparation methods with slow pyrolysis results, similar trends are achieved for the same copper loadings. The increase in copper loading ratio in catalyst has a small but negative effect on the pyrolysis bio-oil yields for both catalysts. It can also be seen that the gaseous product without catalyst (35.92%) decreases to 34.09% with use of CP1.

3.3. Characterization of bio-oils

3.3.1. Elemental analysis of bio-oils

An essential parameter to compare products derived from thermal processes is the elemental composition. Elemental composition of bio-oils, O/C and H/C molar ratios, higher heating values (HHV) obtained under different pyrolysis conditions are given in Table 2. The carbon content of catalytic pyrolysis bio-oils is greater than that of non-catalytic pyrolysis. When a catalyst is used, hydrogen content of oil increased for both slow and fast pyrolysis. The oxygen content of bio-oils obtained from catalytic fast pyrolysis is very low when compared

Table 2
Elemental analysis results of bio-oils.

	Slow pyrolysis					Fast pyrolysis				
Component	NC	SG1	SG2	CP1	CP2	NC	SG1	SG2	CP1	CP2
C	53.54	55.69	56.97	56.36	53.78	64.93	69.27	67.30	65.51	65.97
H	7.52	8.44	8.85	8.53	8.04	8.30	10.44	10.09	9.63	9.69
N	3.61	3.60	3.61	3.59	3.59	3.56	3.55	3.53	3.53	3.52
O[a]	35.33	32.27	30.57	31.52	34.59	23.21	16.74	19.08	21.33	20.82
H/C	1.69	1.82	1.86	1.82	1.79	1.53	1.81	1.80	1.76	1.76
O/C	0.49	0.43	0.40	0.42	0.48	0.27	0.18	0.21	0.24	0.24
HHV (MJ/kg)	22.59	25.19	26.52	25.68	23.55	29.75	35.47	33.88	32.20	32.54

[a] Estimated by difference.

with liquid products obtained from catalytic slow pyrolysis. Oxygen removing as CO_2 minimizes the exterior H_2 necessity and enhances the H/C ratio in the final products. Oxygenates can be catalytically cracked at 300–500 °C to produce liquid hydrocarbons, whenever the oxygen removed in the form of H_2O, CO, and CO_2 and coke [40]. Due to higher oxygen content, the bio-oils obtained from catalytic slow pyrolysis have lower calorific values and strong corrosive properties.

For the H/C ratios of bio-oils, it can be seen that catalytic pyrolysis gave higher ratios than non-catalytic pyrolysis. H/C ratio is increased from 1.69 up to 1.86 for slow and from 1.53 up to 1.81 for fast pyrolysis. Co-precipitated catalysts used pyrolysis bio-oils have lower H/C ratios than sol–gel used ones. Furthermore comparison of bio-oils' H/C ratios with conventional fuels denoted that ratios obtained in this study lie between light and heavy petroleum products. Moreover the energy density of non-catalytic bio-oils was improved, as indicated by the calculated higher heating values (HHVs) of the bio-oils.

3.3.2. *Functional groups of bio-oils*

FT-IR analysis is an advantageous technique for the attribution of various functional groups. Bio-oils from biomass pyrolysis include a very wide range of complex organic chemicals which cannot be exactly determined in details [41].

FT-IR results of bio-oils obtained under different conditions are summarized in Table 3. According to the spectra, it is seen that the O–H stretching vibrations between 3500 and 3100 cm^{-1} showed the presence of phenols and alcohols for non-catalytic pyrolysis. When catalytic pyrolysis is compared to non-catalytic pyrolysis, it can be seen significant changes in the FT-IR results due to effect of catalyst. The O–H stretching vibration band at 3335 cm^{-1} is almost disappeared for all catalytic bio-oils. This proves the removal of oxygen from raw material during pyrolysis which simultaneously caused the cracking of phenolic and aromatic structures to produce carbonaceous solid products. The C–H stretching vibrations between 2900 and 2800 cm^{-1} and C–H deformation vibrations between 1450 and 1350 cm^{-1} indicated the presence of alkanes. Furthermore, the location of bending vibration of C–H groups at 1375 cm^{-1} provided another evidence of the fact that this band was critical for the detection of methyl groups. The peaks between 1675 and 1575 cm^{-1} represented C=C stretching vibrations which indicated the presence of aromatics and alkenes. The C=O stretching vibrations between 1780 and 1680 cm^{-1} represented the presence of aldehydes or ketones. The presence of both C=O and O–H stretching vibrations also illustrated the presence of carboxylic acids and derivatives [42]. The region between 800 and 650 cm^{-1} contained various bands associated with the aromatic, out of plane C–H bending. The high intensity of above mentioned bands indicated that the aromatic hydrogen was located in aromatic rings with high degree of substitution. The band occurred at 1450 and 1375 cm^{-1} in non-catalytic fast pyrolysis bio-oil's FT-IR spectrum indicated higher content of CH_3 groups in the form of aliphatic chains [42,43]. It was seen that all the pyrolytic oil restrained similar functional groups with a variation in intensity. Thus, FT-IR spectra's of fast and slow pyrolytic bio-oils were very similar to each other.

3.3.3. *GC/MS results of bio-oils*

Due to the complex and heterogeneous nature of bio-oil, gas chromatography/mass spectrometry has become an acceptable, quick and impressive tool for bio-oil characterization [44]. Fig. 6 indicates GC–MS chromatographs of bio-oils obtained by non-catalytic/catalytic slow and fast pyrolysis. Table S1 shows an exhaustive component analysis of the bio-oil samples, including the compound name, molecular formula, and the peak area. Every compound has been graduated as aromatic (Ar), non-aromatic (NAr), oxygenated aromatic (ArO) or

Table 3
FT-IR analysis of pyrolytic bio-oils.

		Slow pyrolysis					Fast pyrolysis				
Functional groups	Wave numbers (cm^{-1})	NC	SG1	SG2	CP1	CP2	NC	SG1	SG2	CP1	CP2
O–H stretch	3500–3100	+	–	–	–	–	+	–	–	–	–
C–H aromatic	3100–3040	+	+	+	+	+	+	+	+	+	+
C–H aliphatic	2950–2800	+	+	+	+	+	+	+	+	+	+
C=O	1770–1650	+	+	+	+	+	+	+	+	+	+
C=C olefinic	1625–1590	+	+	+	+	+	+	+	+	+	+
C=C aromatic	1600,1580,1450	+	+	+	+	+	+	+	+	+	+
C–H aliphatic CH_3	1450 and1375	+	+	+	+	+	+	+	+	+	+
C–H aliphatic CH_2	1465	+	+	+	+	+	+	+	+	+	+
C–O–C unsaturated ethers stretching	1275–1200	+	+	+	+	+	+	+	+	+	+
C–H distortion	1200–1000	+	+	+	+	+	+	+	+	+	+
C–O–C aliphatic ether/primary or secondary alcohol	1060–1020	+	+	+	+	+	+	+	+	+	+
Aromatic rings	900–700	+	+	+	+	+	+	+	+	+	+

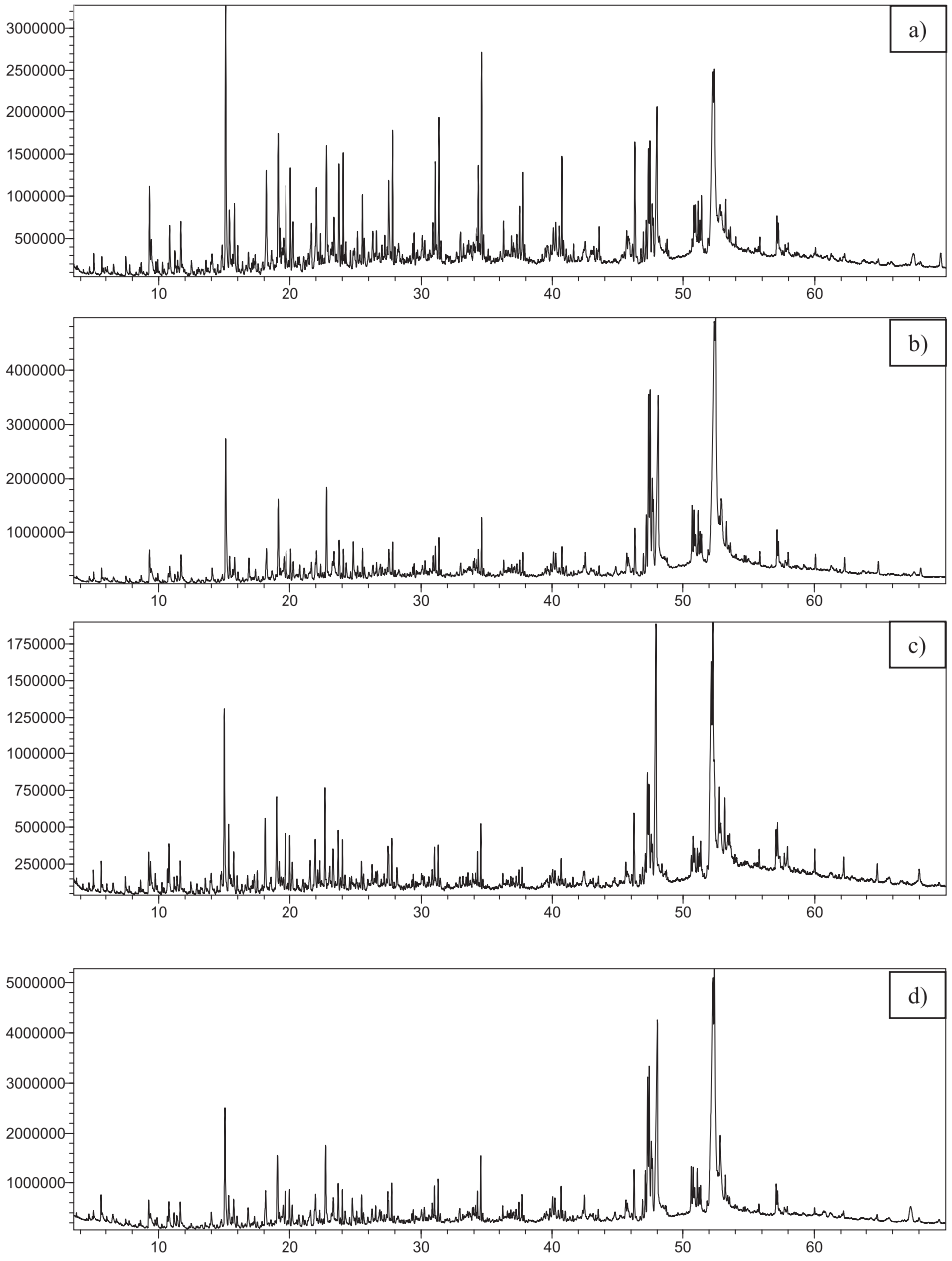

Fig. 6. GC–MS chromatographs of bio-oils obtained by pyrolysis: a) non-catalytic slow pyrolysis, b) non-catalytic fast pyrolysis, c) CP1 catalyst used slow pyrolysis, d) CP1 used fast pyrolysis.

oxygenated non-aromatic (NArO). Table S1 illustrated that various compounds like hydrocarbons (alkanes, alkenes), aromatics with a single ring (benzene, toluene and alkylated derivatives), phenols and alkylated derivatives, carboxylic acids, carbonyls, polycyclic aromatic compounds (PAH) such as naphthalenes, alcohols and furans found in the oil products. As tomato waste was being lack of homogeneous structure, it was transformed into several chemicals which had low yield. During thermal decomposition, molecular chains of the complex compounds in the tomato waste were broken, while developing compounds with a carbon number range of 5–44. Bio-oils are found as similar to each other by means of their aliphatic contents like alkanes and alkenes (dodecane, pentadecane, hexadecane, tridecane, 1-dodecene, 1-decene, 1-tetradecene, 1-tridecene, 3-heptadecene, heneicosane, and hexacosane) [45]. The straight chain of alkanes and alkenes carbon range is observed as C_8–C_{26} for slow pyrolysis bio-oils, while it is C_9–C_{26} for fast pyrolysis bio-oils.

Other most significant compounds in bio-oils are phenolic compounds developed during lignin degradation which consist of phenol, 2-methyl phenol, 4-methyl phenol, 2,3-dimethyl phenol, 2,4-dimethyl phenol, and 3-ethyl phenol. The total phenolic compounds reached its maximum value for non-catalytic slow pyrolysis bio-oils with a percentage of 21.7. This percentage decreased to 16.64 with increasing heating rate. The phenolic compounds decreased with the presence of catalyst and with the copper ratio increment from 5 to 10%. This decrease indicates that the secondary thermochemical decomposition reaction rates transcended the rates of primary thermochemical reactions [46]. Table S1 shows that there are certain polycyclic aromatic hydrocarbons (PAH) such as naphthalene and alkylated naphthalene in the bio-oils. It can be seen that naphthalenes and alkylated naphthalenes are only present in slow pyrolysis bio-oils. Precious aromatics such as toluene and benzene are noticed especially in slow pyrolysis bio-oils. Bio-oils are known to have an acidic structure. The presence of

acids in the bio-oils is undesirable because of their corrosive effects [44]. Carboxylic acids and carbonyl compounds such as pentadecanoic acid, 9,12-octadecadienoic acid, methyl ester-9-octadecenoic acid, and cis-9-hexadecenal with peak areas around or greater than 2% are observed in the GC–MS data. The presence of acidic compounds appeared in low percentages in tomato waste bio-oils which can be qualified as promising in terms of the ultimate fuel quality.

4. Conclusion

The results were compared with those obtained in catalytic and non-catalytic slow and fast pyrolysis. Experimental results indicated that tomato waste as a biomass material is suitable for conversion into liquid and gaseous products.

Comparison of product yields for non-catalytic slow and fast pyrolysis showed that higher bio-oil yield (26.68%) was obtained when heating rate increased from 40 °C/min to 100 °C/min. Lower solid product (26.07%) and higher gaseous product (35.92%) yields were also achieved under fast pyrolysis conditions. Bio-oil yield decreased, gaseous product yield increased as the copper loading ratio increased from 5 to 10% in the catalytic pyrolysis experiments. Optimum copper loading ratio was determined as 5 wt.% for both heating rates. Compared to non-catalytic and catalytic/slow and fast pyrolysis, the catalytic slow pyrolysis of tomato waste resulted in lower bio-oil yields due to catalytic cracking of bio-oil compounds to gaseous products. The bio-oil yield achieved a maximum of 30.31% when 5 wt.% Cu/Al_2O_3 catalyst prepared by co-precipitation method was used with a heating rate of 100 °C/min.

Finally, the results of the spectroscopic and chromatographic methods and the yields of the pyrolysis experiments showed that bio-oils obtained in the presence of Cu/Al_2O_3 catalyst could be utilized in the production of many chemical feedstock and fuels.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.joei.2017.01.010.

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