Research Article

Wei Zhang, Hongying Xia*, Yong Deng*, Qi Zhang, and Chunfu Xin

Slow pyrolysis of waste navel orange peels with metal oxide catalysts to produce high-grade bio-oil

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Abstract: Renewable biomass resources have become increasingly attractive in recent years. In this study, the pyrolysis of waste navel orange peels was carried out with different metal oxides (Cu_2O , CaO , V_2O_5 , Fe_2O_3 , and ZnO) in a tube furnace to obtain high-quality bio-oil, from which high-value chemicals such as 3-furaldehyde could be well recovered to enhance the economic value of waste navel orange peels. The effects of different metal oxides on bio-oil were analyzed by GC/MS. The results showed that Cu_2O and Fe_2O_3 , as catalysts for slow pyrolysis, promoted the production of 3-furaldehyde compounds at a scale of approximately 5.69 and 4.82 times higher than that of pyrolysis without the addition of metal oxides, respectively. High-value chemicals such as 3-furaldehyde obtained from bio-oil can enhance the economic value of waste navel orange peels for full recovery and reuse.

Keywords: navel orange peels, slow pyrolysis, metal oxides, biomass, 3-furaldehyde

1 Introduction

Increasing demand for chemicals and fuels, driven by factors including the scarcity of fossil resources, overpopulation, and the threat of global warming, strains our resources [1]. Finding a path to sustainable development is especially important. Around the world, agricultural production generates large amounts of waste, of which fruit waste is a renewable and sustainable resource, widely available and inexpensive, and often with low recycling rates. In 2017, the world produced about 73.31 million tons of oranges, which is the most abundant fruit crop in the world. China accounts for 10.5% of global production, and annual production continues to increase [2]. In 2006, 33 million tons of oranges were processed into orange juice in the food industry, which resulted in the production of 20 million tons of waste orange peel [3]. Navel orange peels are a potential biomass due to its high content of cellulose, hemicellulose, and lignin [4,5]. Currently, there are three common methods of treating waste navel orange peels, namely, composting, landfilling, and open burning. However, these methods cause various environmental problems. Unpleasant odors released during composting can lead to a decrease in air quality [6]. Landfills will cause greenhouse gas emissions, global warming, and the release of toxic compounds that may have serious health effects on humans. The production of bioethanol from fruit waste is often expensive due to the high energy required in pretreatment applications, such as steam explosions [7].

With the development of pyrolysis technology, it is feasible to convert agricultural wastes into energy and chemicals through thermal treatment. In the thermochemical conversion process, there are four process options as follows: pyrolysis, gasification, direct combustion, and liquefaction. Pyrolysis is considered a promising technology for bio-oil and biochar [8]. Pyrolysis technology has reportedly demonstrated good performance in converting biomass (such as coffee shells [9] and straws [10]) into value-added products such as H_2 gas and biofuels. It also shows that it is

* **Corresponding author: Hongying Xia**, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China; Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming 650093, China, e-mail: hyxia81@163.com

* **Corresponding author: Yong Deng**, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China; National Engineering Laboratory of Vacuum Metallurgy, Kunming 650093, China, e-mail: dengxinuo@126.com

Wei Zhang, Qi Zhang, Chunfu Xin: Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China; Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming 650093, China

effective in converting microalgae [11] and oil palm shell [12] into biofuels. These biomass materials are thermally cracked and decomposed in an inert environment to produce pyrolysis products comprising biochar, bio-oil, and gases containing H_2 , syngas, and light gaseous hydrocarbons. Gaseous products (e.g., H_2 , CO, and C_nH_m) can be used as fuel in gas engines or fuel cells [13,14]. Bio-oil can be used as a chemical feedstock or upgraded to a transport fuel based on its composition [15,16]. Bio-oil, which is a pyrolysis product, is usually a dark brown organic flowing liquid that has a higher calorific value than the raw material and can be easily stored and transported. It can be used in the production of chemicals and is a possible replacement for fuel oils for heating or power generation in many stationary applications [17]. However, it has a high oxygen content, remarkable acidic character, and chemical instability [18]. Thus, bio-oils are low-quality fuels that cannot be used in conventional gasoline. Catalytic cracking is a convenient method for upgrading bio-oil. It can be just an interesting approach for product selectivity [19]. For example, removal of oxygenated groups increases the calorific value, lowers the viscosity, and improves stability. Zeolite cracking of pyrolysis oils has also been studied widely [20], but the liquid yields were found to be low. A large number of scholars have studied the effects of metal oxides on biomass. ZnO inhibits the formation of aromatic hydrocarbons and favors oxygen-containing aromatic compounds [21]. CaO makes that acidity and oxygen content remarkable decrease [22]. Fe_2O_3 is good for hydrogen production [23]. Malani et al. used a Cu_2O catalyst to synthesize biodiesel [24]. Biochar can be used as a smelting raw material, and in the steel smelting industry, biochar can achieve the same sintering yield and sintering productivity as coke powder, and the composite material of coke and biochar can increase the coal replacement rate up to 60% [25]. Currently, considering that metal oxides show good performance in pyrolysis of biomass, this article proposes the use of metal oxide catalysts to slowly pyrolyze waste navel orange peels to produce high grade bio-oil to add value to the waste navel orange peels. The main reason for using slow pyrolysis is that the required temperature is low, which does not lead to the reduction in metal oxides, and the slow pyrolysis can prolong the reaction time, which is helpful for the adequate contact between metal oxides and waste navel orange peels.

In this work, (i) we explore the effect of several metal oxides on the yield of navel orange peel pyrolysis products at suitable temperatures; (ii) we characterize the effect of different metal oxides on bio-oil composition and analyze their differences to determine their respective advantages; and (iii) we characterize the effect of different metal oxides on gas product composition.

2 Material and methods

2.1 Materials

Navel orange peels were collected from the Kunming fruit market, Yunnan, China. The raw materials were crushed to a size of 0.15–0.3 mm and washed thoroughly with distilled water. Then, the samples were dried at 60°C for 24 h and collected for further experiments.

2.2 Slow pyrolysis of navel orange peels

Analytical-grade Cu_2O and CaO were purchased from Shanghai Macklin Biochemical Co., Ltd. Analytical-grade Fe_2O_3 was purchased from Shanghai Shanpu Chemical Co., Ltd. ZnO and V_2O_5 of analytical grade were purchased from Tianjin Ruijinte Chemical Co., Ltd. The mixing ratio of Cu_2O , CaO, Fe_2O_3 , ZnO, V_2O_5 , and navel orange peels was 9 g:4.5 g. The navel orange peel and five metal oxides were mixed with each other using a mechanical mixing method in a JT thermostat steam bath vibrator (ZD-85) oscillating for 20 min at room temperature and rotating at 400 rpm to allow uniform mixing.

12 g of navel orange peel was weighed at a time and slowly pyrolyzed at 50°C intervals in the temperature range of 450–650°C. The optimal pyrolysis temperature of 500°C was determined. In the experimental device, 12 g of the mixed material of navel orange peel and metal oxide was added each time, and the catalytic cracking reaction was carried out at a pyrolysis temperature of 500°C. The vapor exiting the tube furnace passes through two consecutive condensers (both using a water/ethanol mixture at –5°C) where condensable vapors (including organic components and water) were collected. Noncondensable gas (including N_2 , H_2 , CO, CO_2 , CH_4 , C_2H_2 , and C_2H_4 gas) was collected in the airbag, at a heating rate of 25°C·min^{–1}, the incubation time was 60 min.

The yield of the liquid product was obtained by dividing the total weight difference of the condenser before and after the reaction by the initial weight of the biomass. The solid yield was also calculated using the weight difference of the quartz reactors filled with biomass and catalyst after and before the pyrolysis reaction divided by the weight of the initial biomass. The following section describes the method used to calculate the gas production.

2.3 Elemental and ultimate analysis

The elemental analysis was carried out with a Vario EL III analyzer to determine the weight fractions of carbon,

hydrogen, and nitrogen. The weight fraction of oxygen was calculated by difference. The remaining moisture content was obtained by weight loss at 105°C for 12 h, and the ash residue was obtained by thermogravimetry. Thermogravimetric analysis (TGA) was used to determine the weight loss of the biomass sample according to the following procedure: 20 mg of navel orange peels were heated at 10°C·min⁻¹ from 25°C to 800°C in 60 mL·min⁻¹ Ar and held at 800°C for 30 min to remove all volatiles. Finally, 60 mL·min⁻¹ air was introduced at 800°C for 30 min. The final weight of the sample was utilized to calculate the ash content.

The higher heating value (HHV) was calculated according to the equation [26]:

$$[\text{HHV (MJ} \cdot \text{kg}^{-1})] = 0.335 \times \text{C} + 1.423 \times \text{H} - 0.154 \times \text{O} - 0.145 \times \text{N} \quad (1)$$

where C – carbon, H – hydrogen, N – nitrogen, and O – oxygen.

2.4 Thermogravimetry

Lab-scale experiments were performed in a STA449F3 microprocessor-controlled TG/DTG system assisted by a Data Station. The sample mass was 20.0 ± 0.1 mg for each experiment. All runs were carried out under dynamic conditions with a nitrogen flow of 60 mL·min⁻¹ and heating rates of 25°C·min⁻¹ and a temperature range from room temperature to 1,000°C.

2.5 Bio-oil characterization

Detection and identification of the bio-oil composition collected in the condenser was performed on a TRACE 1310 gas chromatography (GC) and ISQ LT mass spectrometry (MS) detector. A capillary column (TG-5MS 30 m × 0.25 mm × 250 μm) was used in combination with the carrier gas at a flow rate of 1:1 mL·min⁻¹ and bio-oil sample diluted with methanol to a dilution factor of 5 and filtered before use by a 0.2 μm PTFE filter. The inlet of the GC was set to 280°C, and the split ratio was 30:1. The mass spectrometer operates in electron ionization mode, and the spectra range from *m/z* to 30–500.

2.6 Gas yield

The gaseous product was analyzed offline using a TCD-equipped micro-GC (TG-BOND Q), Which was set at 80°C

to detect H₂, CO, CO₂, and CH₄ with nitrogen as the carrier gas in the column. A gas flow meter was used to assess the total gas flow to the airbag. This, together with the composition analyzed by the micro gas chromatogram, provides the exact volume percentage of each gas in the mixture. The ideal gas law was utilized to calculate the molar amount of each gas.

3 Results and discussion

3.1 Elemental analysis

The elemental analysis information of the navel orange peel with its components is shown in Table 1, O – 52.67% was obtained by difference (100% – [C% + H% + N%]). Based on the elemental analysis, the empirical formula of the orange peel is determined to be CH_{1.51}O_{0.98}. The moisture content was measured at 130°C, while the HHV = 12.355 MJ·kg⁻¹ was determined by the elemental composition [27]. Table 2 presents the comparison with other researchers. The oxygen content and the ratio between carbon and hydrogen in the orange peel sample are higher than those in the other biomasses.

3.2 TGA

Figure 1 represents six TG curves of the navel orange peel with different metal oxides. Figure 2 represents six derivative thermogravimetric analysis (DTG) curves of the navel orange peel with different metal oxides. Figure 3 represents six differential scanning calorimetry (DSC) curves of the navel orange peel with different metal oxides. Four stage weight loss is observed. For example, the TG curve of the raw material shows the first stage between 30°C and 153°C that represents a weight loss of 4.26 wt%. The second stage located between 153°C and

Table 1: Slow pyrolysis of navel orange peel at different temperatures

<i>T</i> (°C)	Solid (wt%)	Liquid (wt%)	Gases (wt%)
450	27.83	30.67	41.5
500	26.92	32.60	40.48
550	25.83	27.75	46.42
600	25.17	27.07	47.76
650	25.16	19.50	55.34

Table 2: Elemental and proximate analysis of air-dried orange peel (wt%)

Sample	C	H	N	O	Moisture	FC	Ash	HHV (MJ·kg ⁻¹)	Ref.
Navel orange dry peel	40.34	5.08	1.91	52.67	3.47	22.77	3.91	12.355	This work
Soursop seed cake	50.9	5.9	2.5	39.4	6.0	7.5	1.3	19	[2]
Paulownia wood	44.73	6.12	0.87	48.27	6.5	20.64	1.06	20.7	[28]
Citrus waste	47.7	5.2	1.3	45.5		24.8	2.0	18.4	[29]
Walnut shells	52.15	5.77	0.28	41.78	4		0.42	20.51	[30]

C – carbon, H – hydrogen, N – nitrogen, O – oxygen, FC – fix carbon.

289°C represents a weight loss of 33.59 wt%. The third decomposition range is 289–372°C with a weight loss of 21.50 wt%, and the fourth stage located between 372°C and 675°C has a weight loss of 12.86 wt% with 27.79 wt% of the weight of the final solid residue. The average total mass loss is 67.95 wt% within the temperature range of 153–675°C, resulting in a solid residue above 25 wt%. Corresponding to the four stages of weight loss on the TG curves, four peaks are observed on the DTG curves (Figure 3). In the DTG curve of raw material, the first peak is observed at 113°C, the second peak is observed at 221°C, the third at 338.8°C, and the fourth at 571°C.

From the last remaining mass, $\text{Cu}_2\text{O} > \text{V}_2\text{O}_5 > \text{CaO} > \text{Fe}_2\text{O}_3 > \text{ZnO}$. Combined with the DSC and DTG curves, it can be seen that CaO has two more peaks than the other curves and that it is an endothermic reaction. From 415°C to 495°C, the reaction at the first peak is $\text{CaH}(\text{CO}_3)_2$ decomposition. The second peak occurs at a temperature of 663–760°C. The reaction is CaCO_3 decomposition [31]. The CaO reaction reduction process takes place step by step as follows: the following reactions are shown in Eqs. 2–5. The mass loss of the Fe_2O_3 curve from 701°C

to 902°C is significantly different. The reduction occurring at 701–902°C is stronger than that at other temperature ranges. The reaction reduction process takes place step by step: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$. The gradual deoxidation mechanism (H_2 and CO as reducing agents) is described by the following reactions shown in Eqs. 6–12. Guo et al. reported that when the temperature was raised to 820°C, the main iron-containing material was converted to FeO, and when the temperature was higher than 900°C, it was converted to metal Fe. At 980°C, Fe becomes the only iron species, and iron ore can be first reduced by lignin-derived hydrogen and then reduced by CO and carbon [32–35].

The reaction that Cu_2O produces is shown in Eq. 13.

Figure 1: TG curves of dry navel orange peel for different metal oxides in argon atmosphere. **Figure 2:** DTG curves of dry navel orange peel for different metal oxides in argon atmosphere.

Figure 3: DSC curves of dry navel orange peel for different metal oxides in argon atmosphere.

3.3 Effect of temperature on the pyrolysis product yield

Table 1 represents the yields of gas, liquid, and biochar at three different temperatures. From Table 1, it can be seen that as the temperature increases, the biochar yield decreases, liquid production decreases, and gas production increases. When the final pyrolysis temperature increased from 450°C to 650°C, the coke yield decreased from 27.83 to 25.16 wt%. Gas production increased from 41.5 to 55.34 wt%. As the pyrolysis temperature rose from 450°C, the liquid yield increased from 30.67 wt% to a maximum of 32.6 wt% at 500°C. In most cases, lower temperatures (<450°C) favored coke production, while higher temperatures (>600°C) favored natural gas production [36]. At low pyrolysis temperatures, the coke yield was quite high due to the incomplete decomposition of the navel orange peels. As the pyrolysis temperature increased, the production of both liquid and gaseous products increased due to the greater primary decomposition of the feed stock or the secondary decomposition of the carbon residue. The decrease in the liquid yield at a temperature range of 500–650°C can be explained by the secondary reaction of the volatile liquid portion [20,37–39].

3.4 Effect of different metal oxides on the pyrolysis product yield

Table 3 represents the yield of gas, liquid, and solid with five different metal oxides at 500°C. From Table 3, it can be seen that different metal oxides have a large effect on the yields of liquid, solid, and gaseous products. The solid yield is $\text{Fe}_2\text{O}_3 < \text{V}_2\text{O}_5 < \text{Cu}_2\text{O} < \text{CaO} < \text{ZnO}$, and the liquid yield is $\text{CaO} < \text{ZnO} < \text{Fe}_2\text{O}_3 < \text{V}_2\text{O}_5 < \text{without catalyst} < \text{Cu}_2\text{O}$. The solid products were significantly reduced with the addition of Fe_2O_3 , V_2O_5 , and Cu_2O , and the navel orange peel pyrolysis was more complete. It was observed that the yield of bio-oil was increased with Cu_2O , while the liquid products were reduced with the addition of Fe_2O_3 , V_2O_5 , CaO , and ZnO , indicating that these metal oxides were not favorable for liquid production. Zhou et al. reported that adding CaO is not conducive for liquid production [40]. The gas yield is $\text{Cu}_2\text{O} < \text{without catalyst} < \text{ZnO} < \text{CaO} < \text{V}_2\text{O}_5 < \text{Fe}_2\text{O}_3$. In addition, Cu_2O decreases the gas yield, and other metal oxides increase the gas yield.

3.5 Effect of biomass-different metal oxide mixtures on bio-oil

GC/MS has been widely used to detect the composition of bio-oil [41,42]. The main chemical composition of bio-mass oil obtained by slow pyrolysis of waste navel orange peel contains olefins, alkanes, phenols, benzenes, and furans, as shown in Table 4, among which benzenes and furans are still dominant. Figure 4 shows the chromatogram of bio-oil navel orange peels pyrolyzed with mixed CaO . Table 5 represents the comparison of bio-oil

Table 3: Slow pyrolysis of navel orange peel with different metal oxides at 500°C

Catalyst	Solid (wt%)	Liquid (wt%)	Gases (wt%)
ZnO	52.08	30.13	41.75
V_2O_5	48.08	30.75	47.13
Fe_2O_3	47.75	30.5	47.88
Cu_2O	49	36.25	40.25
CaO	52	27.76	44.25
Without catalyst	26.92	32.60	40.48

The liquid rate is calculated: Liquid (wt%) = Liquid quality/Navel orange quality $\times 100\%$; Solid (wt%) = Solid quality/Total quality $\times 100\%$; Gases (wt%) = (Total quality – Solid quality – Liquid quality)/Navel orange quality $\times 100\%$.

Table 4: Bio-oil main components identified by GC-MS in CaO pyrolysis

#	Retention time (min)	Peak area	Compound name	Molecular formula	Chemical structure
1	4.37	6067184.15	Cyclobutene, 2-propenylidene-	C ₇ H ₈	
2	5.92	6674141.81	2-Cyclopenten-1-one	C ₅ H ₆ O	
3	6.30	8668522.44	Ethane, 1,1,1-trimethoxy-	C ₅ H ₁₂ O ₃	
4	6.44	14319733.93	2-Furanmethanol	C ₅ H ₆ O ₂	
5	6.64	27638993.01	Ethylbenzene	C ₈ H ₁₀	
6	6.84	66958567.37	Benzene, 1,3-dimethyl-	C ₈ H ₁₀	
7	7.44	30865650.51	<i>o</i> -Xylene	C ₈ H ₁₀	
8	7.78	1628547.96	2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O	
9	7.90	6496573.64	Butyrolactone	C ₄ H ₆ O ₂	
10	9.03	3650032.94	2-Furanethanol, á-methoxy-(<i>S</i>)-	C ₇ H ₁₀ O ₃	
11	9.22	3237421.50	2-Cyclopenten-1-one, 3-methyl-	C ₆ H ₈ O	
12	9.55	7491222.72	Phenol	C ₆ H ₆ O	
13	10.94	1612239.05	2-Cyclopenten-1-one, 2,3-dimethyl-	C ₇ H ₁₀ O	

(continued)

Table 4: (continued)

#	Retention time (min)	Peak area	Compound name	Molecular formula	Chemical structure
14	11.23	1481137.19	Phenol, 2-methyl-	C ₇ H ₈ O
15	11.67	3232957.84	<i>p</i> -Cresol	C ₇ H ₈ O

components with and without the addition of metal oxides. Table 5 shows that the addition of Cu₂O promoted an increase in the production of benzenes and furans, while the other products decreased. The liquid product with the addition of Cu₂O contained 5.69 times more 3-furaldehyde than other metal oxides. The yield of 3-furaldehyde is Cu₂O > Fe₂O₃ > Non-metal oxide (1 time). 3-Furaldehyde is an important organic chemical feedstock and increasing the content of 3-furaldehyde in bio-oil can increase its recycling value. CaO favors ester production and no acid products, mainly because Ca(OH)₂ produced by the equilibrium Eq. 2 reacts with the production of acidic substances, resulting in the disappearance of acidic substances. Wang *et al.* pointed out that there was no acid production [43]. Veses *et al.* found a decrease in the acidity of bio-oils, consistent with the results in this article [22]. Fe₂O₃ contributes to the production of 2-furanmethanol production. It was thus concluded that the addition of metal oxides has a positive effect on improving the fuel properties of bio-oils.

Figure 4: GC-MS spectrum of the bio-oil from dry navel peel and CaO pyrolysis bio-oil.

3.6 Effect of different temperatures on the gas product composition

Figure 5 represents the content of navel orange peel gas product components at different temperatures. It can be seen from the figure that the content of methane and hydrogen increases gradually with increase in pyrolysis temperature, which can be attributed to the fact that an increase in temperature is conducive to the water gas reaction and hydrocarbon cracking and reforming reaction. The contents of CO and CO₂ first increased and then decreased while reaching their highest levels at 600°C. The significant change in CO and CO₂ concentrations can be attributed to the fact that the self-gasification of coke is stronger than conventional gasification. The main reason is that microwave pyrolysis is selective heating, and the biochar produced by pyrolysis has strong microwave absorption, which leads to the temperature of biochar being higher than other temperatures, which is conducive to the Boudol reaction of carbon.

3.7 Effect of different metal oxides on the gas product composition

Figure 6 shows the effect of different metal oxides on the composition of gas products. ZnO, Fe₂O₃, and V₂O₅ are n-type semiconductors that readily heat and lose oxygen, and the resulting oxygen readily reacts with carbon monoxide. However, ZnO has a weak absorption capacity for CO, so the CO₂ concentration is relatively low. In contrast, CaO and Cu₂O are p-type semiconductors that readily accept O₂, and CaO readily reacts with CO₂ to form calcium carbonate, resulting in a lower CO₂ concentration.

Table 5: Relative content of main components of bio-oil produced by different metal oxides at 500°C

Compound name	Molecular formula	Raw	Cu ₂ O	ZnO	V ₂ O ₅	CaO	Fe ₂ O ₃
Peak area							
<i>E</i> -15-Heptadecenoic acid	C ₁₇ H ₃₂ O ₂	1.00	0.00	0.00	0.70	0.00	0.85
Hexadecenoic acid, 2-(octadecyloxy)ethyl ester	C ₃₆ H ₇₂ O ₃	0.00	1.23	0.00	0.00	0.00	0.00
Toluene	C ₇ H ₈	1.00	0.87	0.73	0.82	0.73	0.87
3-furaldehyde	C ₅ H ₄ O ₂	1.00	5.69	0.00	3.99	0.00	4.82
2-Cyclopenten-1-one	C ₅ H ₆ O	0.00	0.00	3.29	0.00	3.71	0.00
Ethane, 1,1,1-trimethoxy-	C ₅ H ₁₂ O ₃	1.00	0.28	0.41	0.27	0.60	0.40
2-Furanmethanol	C ₅ H ₆ O ₂	0.00	8.14	4.90	6.34	7.95	9.20
Ethylbenzene	C ₈ H ₁₀	1.00	1.19	0.95	1.06	1.03	1.00
Benzene, 1,3-dimethyl-	C ₈ H ₁₀	1.00	1.09	0.85	0.98	0.96	0.95
<i>o</i> -Xylene	C ₈ H ₁₀	1.00	1.20	0.96	1.07	1.06	1.00
2-Cyclopenten-1-one, 2-methyl-	C ₆ H ₈ O	1.00	0.47	0.48	0.44	0.54	0.58
Butanoic acid, 4-hydroxy-	C ₄ H ₈ O ₃	0.00	4.31	2.63	0.00	0.00	4.24
Butyrolactone	C ₄ H ₆ O ₂	0.00	0.00	0.00	3.80	3.61	0.00
2-Furanethanol, á-methoxy-(S)-	C ₇ H ₁₀ O ₃	1.00	0.87	0.41	0.64	0.26	0.49
2-Furancarboxaldehyde, 5-methyl-	C ₆ H ₆ O ₂	1.00	0.66	0.30	0.51	0.00	0.50
2-Cyclopenten-1-one, 3-methyl-	C ₆ H ₈ O	1.00	0.78	0.43	0.85	0.65	0.88
Phenol	C ₆ H ₆ O	1.00	0.87	0.55	0.74	0.64	0.84
Tripropyl orthoformate	C ₁₀ H ₂₂ O ₃	1.00	1.01	1.05	1.27	0.00	0.87
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	C ₆ H ₈ O ₂	1.00	0.48	0.00	0.58	0.00	0.83
2-Cyclopenten-1-one, 2,3-dimethyl-	C ₇ H ₁₀ O	1.00	0.86	0.55	0.78	0.72	0.83
Phenol, 2-methyl-	C ₇ H ₈ O	1.00	1.67	0.50	0.67	0.60	0.85
1-Ethyl-4,4-dimethyl-cyclohex-2-en-1-ol	C ₁₀ H ₁₈ O	1.00	0.00	0.00	0.00	0.00	0.00
<i>p</i> -Cresol	C ₇ H ₈ O	1.00	0.00	0.60	0.69	0.65	0.85
Phenol, 2-methoxy-	C ₇ H ₈ O ₂	1.00	0.00	0.00	0.00	0.00	0.53
Phenol, 3,4-dimethyl-	C ₈ H ₁₀ O	1.00	0.00	0.00	0.00	0.00	0.00
Formic acid, 2,3-dimethylphenyl ester	C ₉ H ₁₀ O ₂	0.00	1.36	0.00	0.00	0.00	0.00
2-Methoxybenzoic acid, 3-phenylpropyl ester	C ₁₇ H ₁₈ O ₃	0.00	0.00	0.00	1.37	0.00	1.45
Catechol	C ₆ H ₆ O ₂	1.00	0.00	0.00	0.00	0.00	0.00
Cyclohexane, 1,1'-dodecylidenebis[4-methyl-	C ₂₆ H ₅₀ O	1.00	0.00	0.00	0.00	0.00	0.00
Hydroquinone	C ₆ H ₆ O ₂	1.00	0.00	0.00	0.70	0.00	0.85
5-(Hydroxymethyl)-2-(dimethoxymethyl)furan	C ₈ H ₁₂ O ₄	0.00	1.23	0.00	0.00	0.00	0.00

Figure 5: Gas distribution at different temperatures. **Figure 6:** Gas distribution of navel orange peel with different metal oxides.

The lower CO emission observed in the presence of CaO can be explained by the enhanced transfer reaction caused by the capture of CO₂ by calcium-based materials [44]. As seen in Figure 5, the addition of Cu₂O, ZnO, and CaO increased the hydrogen content of the gas product, decreased the CO content, and increased the H₂/CO value of the gas product, increasing the reuse value of the gas product. Fe₂O₃ was reduced to Fe₃O₄ and the main body of the catalyst was magnetite, and the catalyst exhibited significant water-gas transfer reactivity, leading to increased CO and H₂ content [23].

4 Conclusion

In this work, an experimental study of slow pyrolysis of waste navel orange peel was conducted to explore the effect of several metal oxides (Cu₂O, CaO, V₂O₅, Fe₂O₃, and ZnO) on the composition of the pyrolysis products. The experimental results showed that the highest yield of liquid products was obtained by slow pyrolysis of navel orange peel at 500°C pyrolysis temperature. Among several metal oxides, the addition of Cu₂O effectively increased the yield of biomass oil, while the addition of Fe₂O₃, V₂O₅, CaO, and ZnO decreased the yield of liquid products, which was not favorable for liquid production. The content of 3-furancarboxaldehyde in the biomass oil obtained by adding Cu₂O pyrolysis was 5.69 times more than that without the addition of metal oxides, and the obtained furan-like high-value chemicals such as 3-furancarboxaldehyde could improve the poor quality of conventional pyrolysis biomass oil and increase the economic utilization of waste navel orange peel. In addition, the variation in gas product composition shows that different metal oxides have different selective catalytic ability for the components in gas products, and Cu₂O, ZnO, and CaO can improve the H₂/CO value of gas products and increase the opportunity of gas product recovery and reuse. Solid product biomass char as a reducing agent can also be used to recover metal oxides (e.g., Fe₂O₃ and Cu₂O), which facilitates the comprehensive utilization of waste navel orange peel pyrolysis products.

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