Enhancing Bio-based Chemical Production and Reducing Pollutants Emission through the Synergistic Effect of ZSM-5/CaO during Hydrogen-deficient Biomass Pyrolysis

Mudassir Hussain Tahir and Naoto Shimizu*

Research Faculty of Agriculture; Field Science Center for Northern Biosphere, Hokkaido University, Sapporo, Hokkaido, 060- 8589; 060-0811, Japan

Corresponding author
Naoto Shimizu
Research Faculty of Agriculture;
Field Science Center for Northern Biosphere,
Hokkaido University, Sapporo,
Hokkaido, 060- 8589; 060-0811, Japan
Email: shimizu@agr.hokudai.ac.jp

ABSTRACT

The study proposed the use of ZSM-5/CaO as a catalyst to simultaneously improve the quality of pyrolytic products and reduce pollutants emission during the pyrolysis of hydrogen-deficient biomass, specifically cabbage waste (CW). Variables such as pyrolysis temperature and catalysts, including 5% ZSM-5, 5% CaO and 10% ZSM-5/CaO, significantly affected biomass conversion, yield, and products composition. Thermogravimetric-Fourier transform infrared spectroscopy (TG-FTIR) analysis shows that the catalysts (5% ZSM-5, 5% CaO and 10% ZSM-5/CaO) reduced pollutants emission and increased value-added chemicals production by 24.96%, 28.5%, 17.39% and 75.04%, 71.5%, 82.1%, respectively compared to non-catalytic process as 34.18% and 65.82%. Moreover, these catalysts enhanced the relative yield of olefins, aromatics, and phenols to 23.5, 21.6, 27.6% for 5wt.%ZSM-5; 20.8, 18.7, 23.3% for 5wt.%CaO; 30.7, 38.6, 41.3% for 10wt.%ZSM-5/CaO, compared to the non-catalytic process' yield of 15.7, 10.7, 19.3%. Py/GC-MS analysis confirms that these catalysts also decreased PAH and oxygenates production to 13.5, 15.3% for 5wt.%ZSM-5; 11.8, 9.1% for 5wt.%CaO; 5.2, 4.7% for 10wt.%ZSM-5/CaO, in contrast to the non-catalytic process' 26.2, 28.7%. This confirms the synergistic effect of ZSM-5/CaO for upgrading bio-based chemicals and reducing pollutants emission.

Keywords: Catalytic pyrolysis, ZSM-5/CaO, Hydrogen-deficient biomass, Bio-chemical Upgradation, Pollutant's reduction.

1. Introduction

Pyrolysis is considered as a promising strategy to convert biomass into value-added chemicals and reduce the environmental impact of fossil fuels [1]. However, low hydrogen contents of biomass results in bio-oil production with undesirable properties such as significant water contents, high viscosity, poor ignition, corrosiveness, low energy density, thermal instability, and higher oxygen contents, which also lead to pollutants emission [2]. Various techniques such as esterification, reactive distillation and hydroprocessing, are commonly applied to upgrade bio-oil. However, while these methods enhance the oil's quality, they also increase production cost and ultimately, lower the overall energy proficiency, challenging their economic viability [3]. In this context, catalytic pyrolysis can be a potentially superior technique for upgrading oil's quality and simultaneously, reducing pollutants emission [4]. The energy conversion efficiency of catalytic pyrolysis surpasses other upgrading methods, mainly because it eliminates condensation steps and energy-intensive re-evaporation [5]. Therefore, catalytic pyrolysis offers an advanced approach to enhance bio-oil's quality and reduce pollutants emission.

To enhance efficiency of catalytic pyrolysis, it is important to optimize the process temperature and design the catalyst in favor of high-quality oil production. The zeolite ZSM-5 plays a essential role in biomass conversion to aromatic hydrocarbons, due to its specific pore structure and distinct acidity [6]. Various studies have shown that ZSM-5 significantly promotes olefins and aromatics production [7], attributed to its steric hindrance, specific pore structure and catalytic activity [8,9]. However, ZSM-5's strong acidity leads to the production of polycyclic aromatic hydrocarbons (PAHs), which are undesirable due to their environmental implications and

carcinogenic properties [10]. To mitigate these challenges, calcium oxide (CaO) has been observed as an alternative catalyst because of its affordability, basicity, non-toxicity, and CO_2 absorption potential [11]. CaO promotes the conversion of acids into hydrocarbon compounds via decarboxylation reactions [12]. Additionally, CaO removes oxygenates in the form of CO, CO_2, and H_2O, and ultimately, enhances oil's stability [13,14]. Importantly, CaO favors aldol condensation and ketonization, marking it as an promising catalyst in this domain [15,16].

Cabbage is an essential vegetable worldwide, yet despite its widespread use, approximately 30% of the harvested cabbage is discarded. This waste, predominantly generated in canteens and supermarkets, constitutes a significant biomass resource. Improper management of cabbage waste (CW) can lead to environmental issues, such as groundwater contamination, bacterial proliferation, and unpleasant odors [17]. Although CW has been utilized to produce energy and chemicals via pyrolysis [18,19], its low hydrogen content limits its effectiveness in producing value-added fuels and chemicals [20].

The study of biomass decomposition is essential for advancing thermochemical conversion technologies. Despite extensive research on biomass and catalytic pyrolysis, the impact of ZSM-5 and CaO blends on hydrogen-deficient biomass (H-DB), such as cabbage waste biomass pyrolytic behavior, is yet to be explored. Thermogravimetric analysis (TGA), a method used to measure weight loss during thermal decomposition, is crucial for modeling pyrolysis [21]. However, for a comprehensive analysis of volatiles produced during pyrolysis, TGA should be integrated with Fourier Transform Infrared (FTIR) spectroscopy [22]. Despite its limitations, the combination of Py/GC-MS and TG-FTIR can provide enhanced accuracy in pyrolysis gas measurements [23].

In this study, we examine the thermal characteristics of H-DB pyrolysis under the influence of ZSM-5, CaO, and ZSM-5/CaO catalysts as well as different heating rates (20°C/min, 30°C/min,

40°C/min, and 50°C/min), as determined by TGA. Furthermore, we also investigate the catalytic pyrolysis process of H-DB using ZSM-5, CaO, and ZSM-5/CaO catalysts through TG-FTIR and Py-GC/MS. This evaluation considers various aspects: (2) thermal decomposition behaviors; (2) product types and their relative yields; and (3) the effect of catalytic pyrolysis on the chemical composition of bio-oil.

The specific objectives of this study are to:

- evaluates the effectiveness of ZSM-5, CaO, and their combination (ZSM-5/CaO) in thermal decomposition of hydrogen-deficient biomass such as CW.
- explores the potential synergistic effects between CaO and ZSM-5 to improve biomass conversion and reduce residue.
- optimize the reaction temperature and investigate the release patterns of volatile compounds by TG-FTIR.
- Examine products composition produced over CaO/ZSM-5 catalyst using Py/GC-MS

2. MATERIALS AND METHODS

2.1 Samples and catalysts preparation

In this experiment, hydrogen-deficient biomass (H-DB) i.e., cabbage waste (CW) was obtained from a local producer in Suzhou, China. The CW was dried at 105°C for 24 hours, ground into a 100-mesh (~250 μm) powder, and stored in a desiccator for future use. The preparation involved mixing 5 g of ZSM-5 zeolite with 100 mL distilled water, adding 5 g of nano-CaO gradually with stirring, and sonicating for 30 minutes. The mixture was dried at 80°C for 12 hours and calcined at 600°C for 3 hours. Proximate and ultimate analysis were performed according to methods reported in a previous study [18]. LECO CHNS-932 analyzer was used for ultimate analysis.

proximate analysis was achieved using ASTM procedures, Moreover, the volatile matters and ash contents were calculated using ASTM standard procedure D5142-09. Finally, three distinct samples with varying weight ratios to biomass were prepared: 5wt.%ZSM-5, 5wt.%CaO, and 10wt.%ZSM-5/CaO.

2.2 Thermogravimetric analysis (TGA)

The thermogravimetric analysis used an SDT Q600 instrument, heating 5-10 mg samples at 800°C under nitrogen for 10 minutes. Subsequently, oxygen was introduced at 5 mL/min to oxidize remaining solids. A constant nitrogen flow of 80 mL/min was maintained for all varying conditions (20, 30, 40, and 50°C/min). Each sample revealed three comparable TG curves, exhibiting a maximum of 1% uncertainty in the final conversion during CW pyrolysis.

2.3 Biomass conversion

The catalytic pyrolysis process generates volatile products, which can be quantified using thermogravimetric (TG) data through Equation (1) for weight basis calculations and Equation (2) for solid residue assessments.

$$\text{Conversion (\%)} = \frac{m_s - m_r}{m_s} \text{x} 100 \qquad \text{Eq. (1)}$$

where m_s, m_r — mass of sample and solid residue (fixed carbon, ash and catalyst)

Solid residue (char, coke) %= 100% - (conversion of biomass% + ash%) Eq. (2)

2.4 TG-FTIR analysis

A thermal analyzer (SDT Q600 instrument) combined with an infrared spectrometer (Bruker Tensor 27 FTIR) was used to identify gases released during pyrolysis. Samples were heated from room temperature to 750°C at 20°C/min in a nitrogen atmosphere, flowing at 80 mL/min. To avoid secondary reactions and gas condensation, gas cells and transfer pipes were

maintained at 200°C. FTIR detection of evolved products provided IR spectra with 1cm^{-1} resolution in the 4000–400 cm^{-1} range.

2.5 Py/GC-MS Analysis

The GC/MS (Agilent 7890B-5977A) was utilized to analyze chemical compounds yields during pyrolysis performed at 500°C. A 4 ± 0.1 mg sample was placed in a 2 cm quartz tube and heated via a platinum filament. Fast pyrolysis performed in a pure nitrogen atmosphere, and products entered the GC inlet. Chromatographic separation employed a metal capillary column, with adjusted temperatures. The ion source temperature was set at 230°C, and the scan range was 33-500 m/z. Peak areas of pyrolysis products were determined using the NIST library and relevant reports.

3. RESULTS AND DISCUSSION

The ultimate and proximate analysis of CW is listed in Table 1. The higher volatile matter contents of CW at 73.61% than other biomasses [24–26] indicates its potential for producing liquid and gaseous products through pyrolysis. With a moisture content of 6.77%,

Table 1. Ultimate and proximate analysis of CW.

Proximate analysis (wt.%)	
Ash	5.01
Moisture	6.77
Volatile matter	73.61
Fixed carbon	14.71
Ultimate analysis (wt.%)	
Carbon	53.88
Hydrogen	4.23
Oxygen	37.17
Sulfur	2.71
Nitrogen	2.01

CW meets the industrial standard for pyrolysis, which requires a moisture content below 10% for optimal product quality and energy efficiency [27]. The ash content of CW is relatively low at 5.01%, reducing the risks of agglomeration, fouling, and slagging, and facilitating mass and heat transfer during pyrolysis [28]. The high carbon content of CW (53.88%) suggests its capability to yield high-quality biochar suitable for catalytic applications [29]. The low nitrogen (N) and sulfur (S) contents, at 2.01% and 2.71% respectively, contribute to the environmental benefits of CW by minimizing the emissions of toxic gases such as SO_x and NO_x [30]. Higher oxygen contents (37.17 %) of CW are linked to the oxygen-rich functional groups presence in its structure (see FTIR analysis in Fig. S1). However, CW's lower hydrogen content compared to other biomasses (see Table 2) may limit its use in bio-based chemicals and fuel production and could lead to increased emissions during thermochemical conversion.

Table 2: Comparison of hydrogen contents of CW with previously reported biomasses.

Biomass	**H (wt.%)**	**References**
Cabbage waste	4.23	Present study
Rice husks	6.62	[40]
Oat straw	6.16	[40]
olive husks	6.96	[41]
pinewood	6.40	[41]
willow, SRC	5.54	[42]
Banana peel	5.67	[43]
Pine bark	5.90	[44]
Wheat straw	6.11	[44]
olive residue	6.82	[42]
Beech wood	5.42	[45]
Pine needles	7.08	[46]
Pinewood sawdust	6.06	[47]
Mango peel	5.17	[29]
Douglas fir	6.91	[48]
Pine sawdust	6.04	[49]
Twigs	5.88	[50]
Empty Fruit Bunches	6.31	[51]

To address this, we proposed catalytic pyrolysis using ZSM-5/CaO to enhance the quality of pyrolytic products and reduce pollutant emissions. This approach ensures the efficient utilization of CW in energy and chemical production while maintaining eco-friendly practices.

3.1 Effect of catalysts on the thermal degradation and product relative yield of CW.

Fig. 1(a&b) shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for cabbage waste (CW) with and without catalysts, using a 20°C min^{-1} heating rate and an 80 mL/min flow rate. CW's thermal degradation occurs in three main phases.

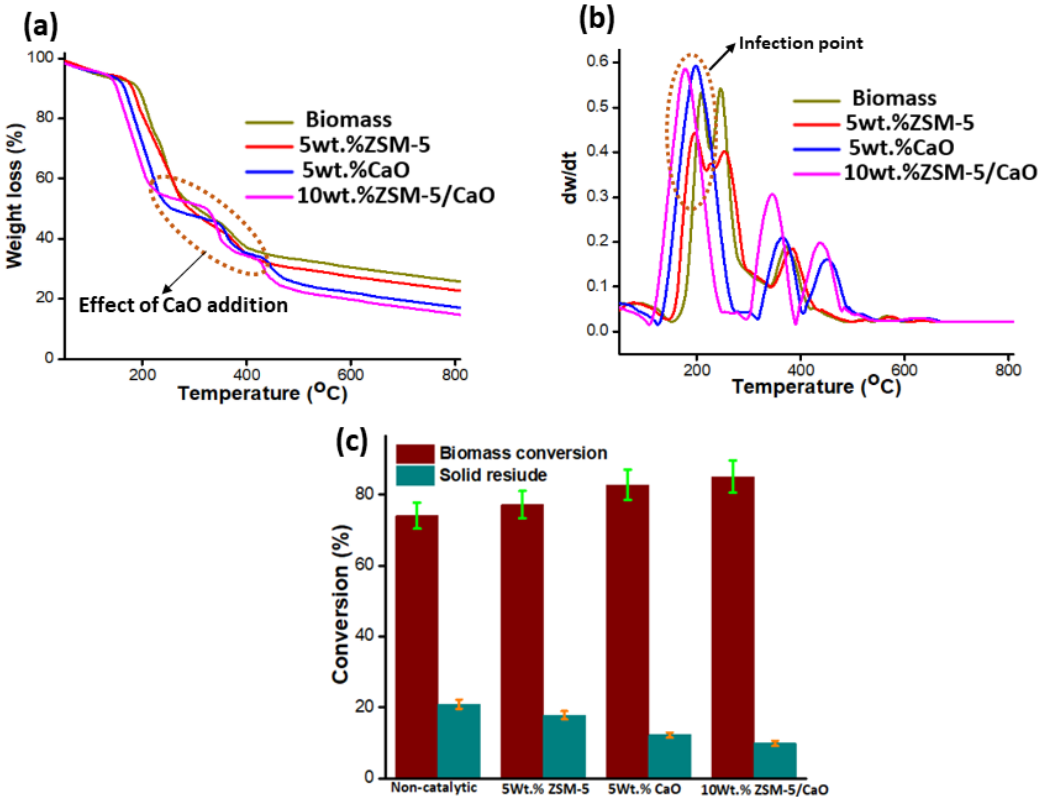

Fig. 1. Effect of ZSM-5, CaO and ZSM-5/CaO on (a) TGA analysis (b) DTG analysis and (c) Biomass conversion and residue formation.

The first phase (30-115°C) is due to moisture evaporation; the second phase (140-410°C) involves the breakdown of hemicellulose, cellulose, starch, lignin, and protein through various chemical reactions. The last phase (425-800°C) involves pyrolysis of remaining components [31]. The non-catalytic inflection point (maximum weight loss rate) is 213.7°C; with catalysts, it lowers to 201.5°C, 193.8°C, and 176.3°C for 5wt.%ZSM-5, 5wt.%CaO, and 10wt.%ZSM-5/CaO, respectively (Fig. 1b). The TG and DTG curves for 5wt.%ZSM-5 pyrolysis is similar, but

5wt.%CaO catalysts differ from non-catalytic pyrolysis. As shown in Fig. 1a, two additional stages occur due to CaO in the CW pyrolysis process and this suggests that cellulose and hemicellulose decomposition primarily happen below 400°C. In the second stage, CaO absorbs released CO_2, delaying mass reduction compared to pure CW pyrolysis. The fourth stage takes place above 500°C, with $CaCO_3$ decomposing into CaO and CO_2, causing a rapid weight decrease and a small peak. The generated CO_2 reacts with biochar at relatively high temperatures, enhancing biomass conversion [32]. The impact of catalysts on the yield of volatile products and solid residue is demonstrated in Fig. 1c. It reveals that the yield of volatile products and solid residue for non-catalytic pyrolysis is 74.08% and 25.92%, respectively. The conversion of CW exhibited an increase from 74.08% to 77.15%, 82.87%, 85.08%, while the residue decreased from 20.91% to 17.85%, 12.22%, and 9.91% with the addition of 5wt.%ZSM-5, 5wt.%CaO, and 10wt.%ZSM-5/CaO, respectively. The results suggest that 10wt.%ZSM-5/CaO, when used as a catalyst, promoted the production of volatile substances with a peak rate of 85.05% and reduced residue formation to 9.91%, making it an ideal candidate for biomass pyrolysis.

The sample's temperature change during pyrolysis can be determined using TG-FTIR analysis. FTIR data can also predict gas constituents and their relative yield [33]. Ultimately, relative yield of these evolved gases was calculated by integrating the FTIR profile at different temperature and different mass ratio of catalyst. The specific wavenumber of the volatiles (value-added chemicals and pollutants) used to examine their releasing pattern and ascertain their production during CW pyrolysis process is given in Table 3.

Table 3. Specific wavenumbers of evolved volatiles for FTIR analysis from CW pyrolysis [31,52–55].

Chemical compounds	Wavenumber (cm^{-1})
Non-condensable volatiles (pollutants)	
CO_2	2306
CH_4	2937
SO_2	1342
CO	2179
NO	1762
NH_3	987
Condensable volatiles (value-added)	
Aldehyde	1797
Acids	1289
Olefins	1643
Aromatics)	1510
Alcohols	1156
Phenols	1238

The FTIR spectra of evolved gaseous products during non-catalytic pyrolysis is presented In Fig. S2. While, to optimize temperature for examining the catalyst's impact on the nature and relative yield of pyrolytic products, the gaseous products' FTIR spectra at 400, 500, and 600°C were selected and examined (Fig. 2a). During pyrolysis, a clear inverse correlation exists between non-condensable (pollutants) and condensable (value-added) volatiles. As the former's rises, the latter's decreases, especially noticeable at temperatures of 400°C, 500°C, and 600°C (Fig. 2b). The optimal balance, with the lowest relative yield of non-condensable gases and the highest of condensable gases, occurs at 500°C. In Fig. 2c, it can be observed that temperature significantly impacts the relative yield of pollutant components and value-added volatile components. The presence of alkenes and olefins in condensable volatiles indicates potential for bioenergy and bio-based chemicals production. Alkene derivatives, benzene and toluene, have high heating values (HHVs) of 49.9 and 41.8 $MJkg^{-1}$ respectively comparable to conventional fuels with respective HHVs of 47.3 and 44.8 $MJkg^{-1}$ [34]. D-limonene, a common olefin component, has diverse applications, enhancing its value as a bio-chemical. Non-condensable volatiles, such as CO_2, CH_4, CO, SO_2, SO, NO, NH_3, significantly impact global climate change, posing challenges to

mitigation efforts [22]. Thus, TG-FTIR analysis confirms that 500°C temperature is the optimal due to its ability to lower the relative yield of pollutants while simultaneously increasing the relative yield of both alkene and olefin to 17.85% and 13.87% respectively.

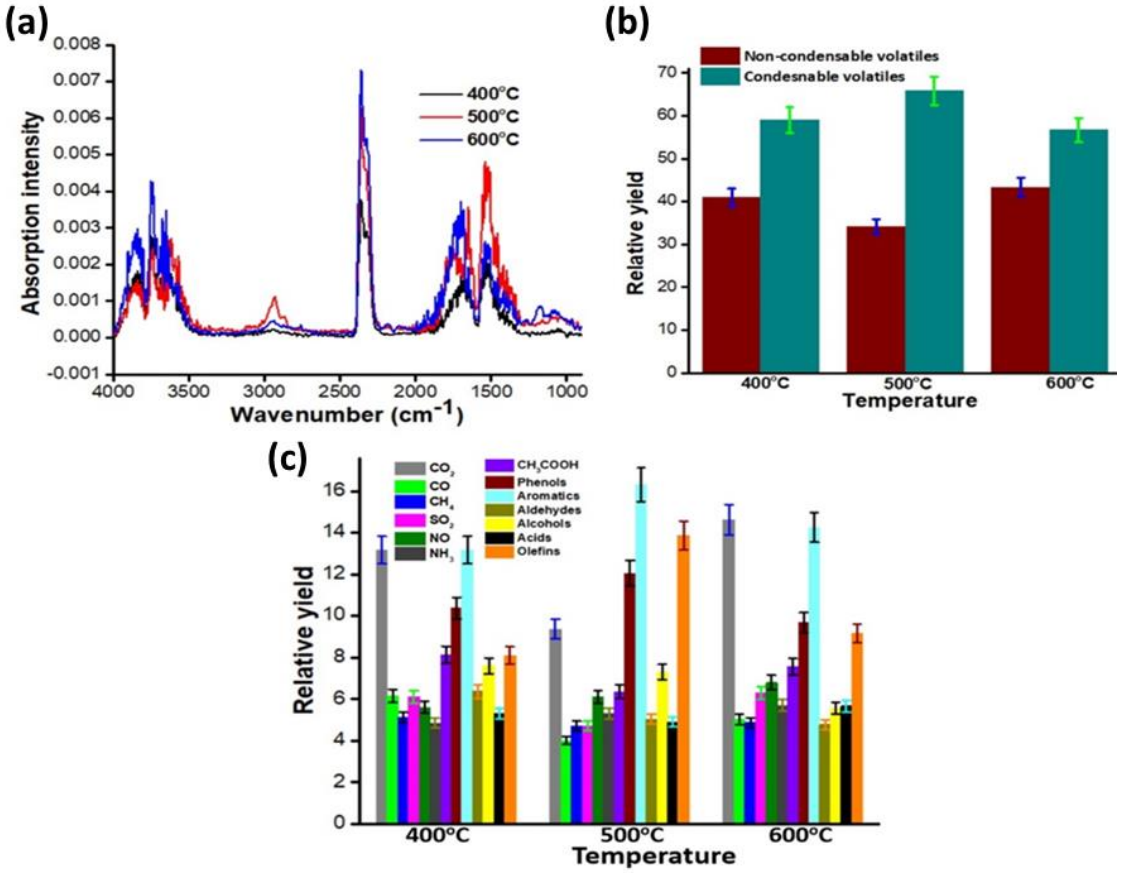

Fig. 2. Effect of temperature on CW pyrolysis, observed at 400, 500, and 600oC. It presents **(a)** the FTIR spectra, **(b)** the relative yield of non-condensable volatiles and condensable volatiles, and **(c)** the relative yield of various volatiles, which includes both condensable and non-condensable volatiles.

In perspective of catalytic efficiency, the ZSM-5 catalyst effectively facilitates deoxygenation by catalytically cleaving and transforming C-O and C-C bonds, allowing for the conversion of oxygen-containing intermediates like CO_2 [35]. In addition, it has been noted that calcium oxide (CaO) decreases both viscosity and oxygen levels. Furthermore, it has been found to absorb CO_2 from the gas phase and fix CO_2-like compounds directly into the liquid product and

thus reduce CO_2 emission, thereby mitigating CO_2 emissions. It also aids in the in-situ deoxygenation process, leading to reduction in oxygen contents. To examine catalytic effects, FTIR spectra during CW pyrolysis with 5wt.%ZSM-5, 5wt.%CaO, and 10wt.%ZSM-5/CaO are shown in Fig. S3. Moreover, FTIR spectra for each pyrolysis process conducted at 500°C are depicted in Fig. 3a. While, Fig. 3b presents the relative yields of both pollutant volatiles and value-added volatiles. Additionally, Fig. 3c illustrates the relative yields of each category of condensable components (value-added volatiles) and non-condensable components (pollutant volatiles).

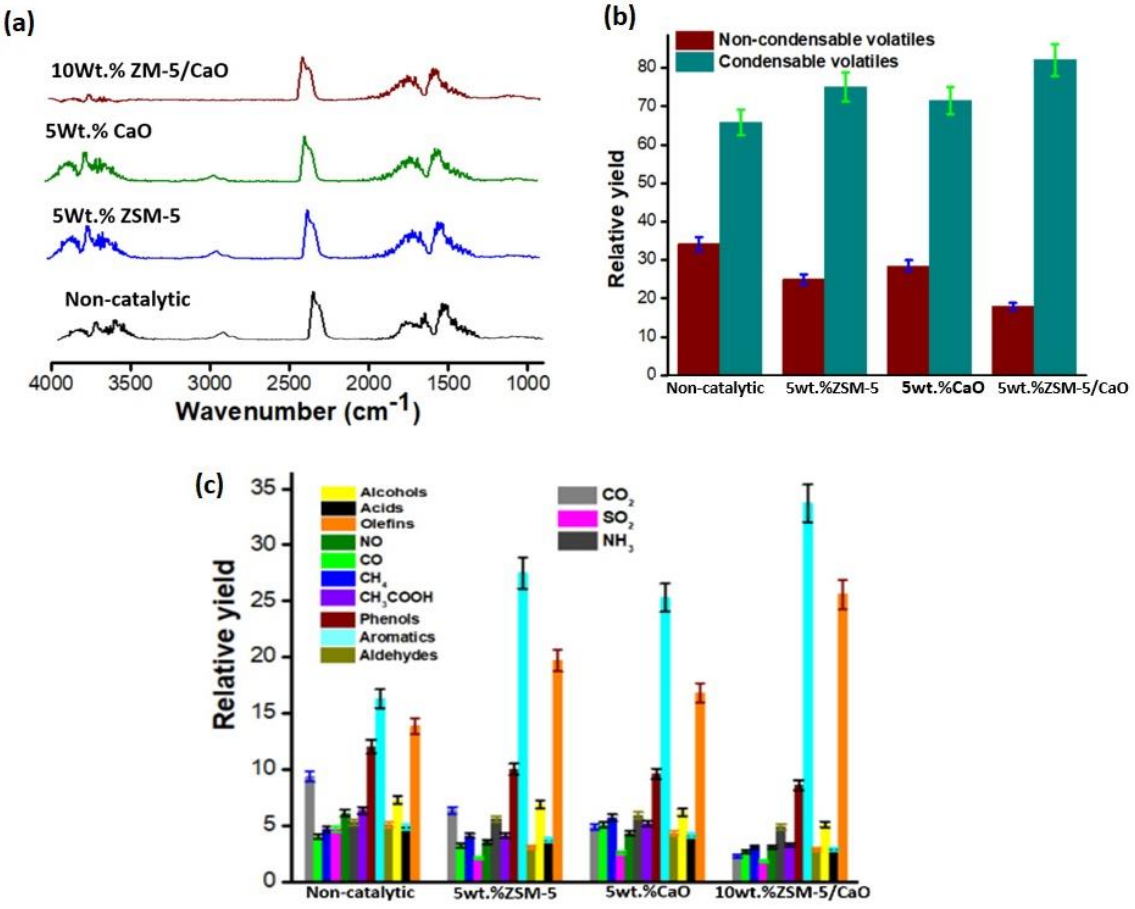

Fig. 3. Effect ZSM-5, CaO and ZSM-5/CaO on CW pyrolysis, observed at 500oC. It presents **(a)** the FTIR spectra, **(b)** the relative yield of non-condensable volatiles and condensable volatiles, and **(c)** the relative yield of various volatiles, which includes both condensable and non-condensable volatiles.

It can be seen from Fig. 3b, the pollutants account for approximately 34.18% of the output, while value-added chemicals make up the remaining 65.82%. However, a different pattern emerges in case of catalytic pyrolysis. Here, the use of 5wt.%CaO and 5wt.%ZSM-5 catalysts correlate with a marked decrease in pollutant emissions, by 28.5% and 24.96% respectively. This reduction is even more pronounced when these catalysts are combined to form 10wt.%ZSM-5/CaO, with pollutant levels dropping to 17.39%. Simultaneously, the production of value-added chemicals appears to increase with the use of 5wt.%CaO and 5wt.%ZSM-5, reaching relative yields of 71.5% and 75.04% respectively. The combined use of these catalysts in the form of 10wt.%ZSM-5/CaO leads to an even more significant increase, with a relative yield of 82.1%. From this analytical perspective, it becomes clear that while 5wt.%CaO and 5wt.%ZSM-5 individually contribute to a decrease in pollutants and an increase in the production of value-added chemicals, their combined use as 10wt.%ZSM-5/CaO amplifies these effects. This suggests a synergistic relationship between the two catalysts that warrants further exploration in future studies.

Fig. 3c presents an in-depth analysis of catalytic effect on the production of value-added chemicals and the reduction of pollutant emissions at 500°C. It was found that the relative yield of aromatics and olefins increased to 33.7% and 25.6% for 10wt.%ZSM-5/CaO as compared to non-catalytic pyrolysis, which yielded 16.3% and 13.87% respectively. In terms of pollutant reduction, the relative yield for CO_2, CO, CH_4, SO_2, NO, NH_3 was recorded as 9.37, 4.01%, 4.7%, 4.5%, 6.1%, and 5.3% in the case of non-catalytic pyrolysis. For 10wt.%ZSM-5/CaO, the relative yield was found to decrease to 2.3%, 2.7%, 3.1%, 1.8%, 3.1%, 4.9%. This fluctuation confirms that 10wt.%ZSM-5/CaO could be efficient in upgrading pyrolytic products and reducing pollutants during the pyrolysis of hydrogen deficient biomass such as CW.

3.2 Effect of heating rate on thermal decomposition

To examine effect of heating rate on thermal decomposing, TGA and DTG analysis of CW pyrolysis with ZSM-5/CaO at heating rates of 20, 30, 40, and 50°C/min are shown in Fig. 4(a&b). As the heating rate increased, both the TG and DTG curves exhibited a shift towards higher temperatures, indicative of thermal hysteresis during pyrolysis [36].

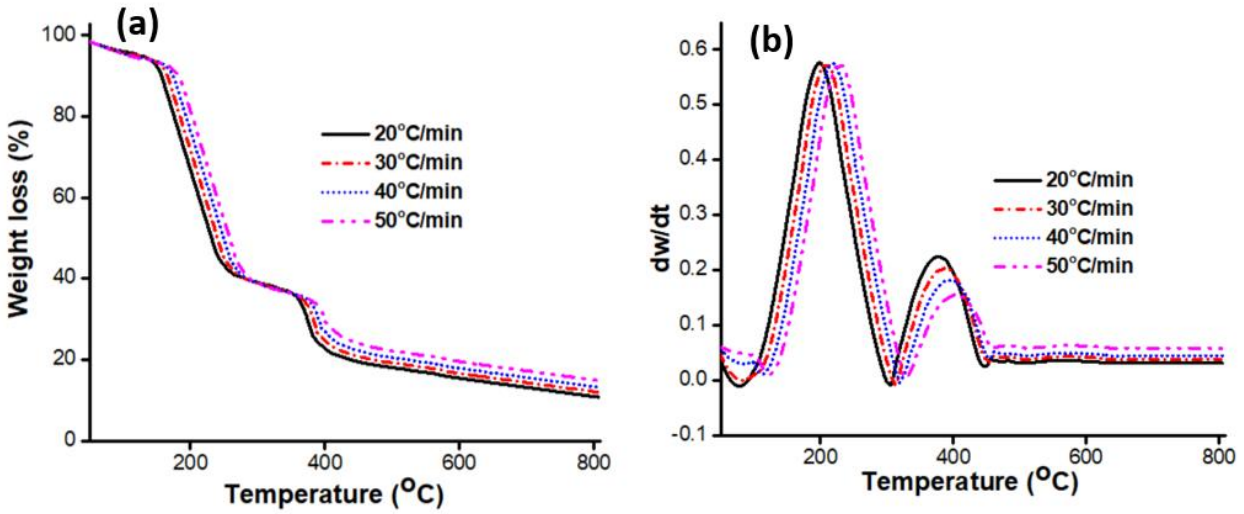

Fig. 4. Effect of heating rate on thermal decomposition of CW with ZSM-5/CaO **(a)** TGA analysis **(b)** DTG analysis

Concurrently, the onset temperature for the release of volatile matter and the peak temperatures on the DTG curves rose with the heating rate. Specifically, at a specific pyrolysis temperature i.e., 800°C, higher residual weights were recorded as 10.85%, 12.03%, 13.28%, and 14.94% for heating rates of 20, 30, 40, and 50°C/min, respectively. The DTG curves also revealed an increase in the maximum rate of weight loss and its associated temperature as the heating rate increased. The variation in characteristic temperatures of biomass pyrolysis at different heating rates is primarily attributed to the heat and mass transfer within and around the biomass particles. At lower heating rates, the uniform internal-to-external heating of the samples allows for a more rapid and efficient pyrolysis, leading to swift weight loss. Conversely, at higher heating rates, the biomass particles

reach the final pyrolysis temperature more quickly, which is favorable for pyrolysis. However, this also results in a greater temperature gradient between the inner and outer surfaces of the biomass particles. While the carrier gas efficiently removes the pyrolysis products from the surface, the interior experiences a lag in heat transfer, which can impede the pyrolysis of inner particles. Consequently, biomass pyrolysis spans a broader temperature range, causing the DTG peak to shift to higher temperatures [37].

3.3 Py/GC-MS analysis

Fig. 5 provides a comparative analysis based on Py/GC-MS analysis resulting from both non-catalytic pyrolysis and catalytic pyrolysis of CW while, raw spectra obtained is shown in Fig. S4(a-d).

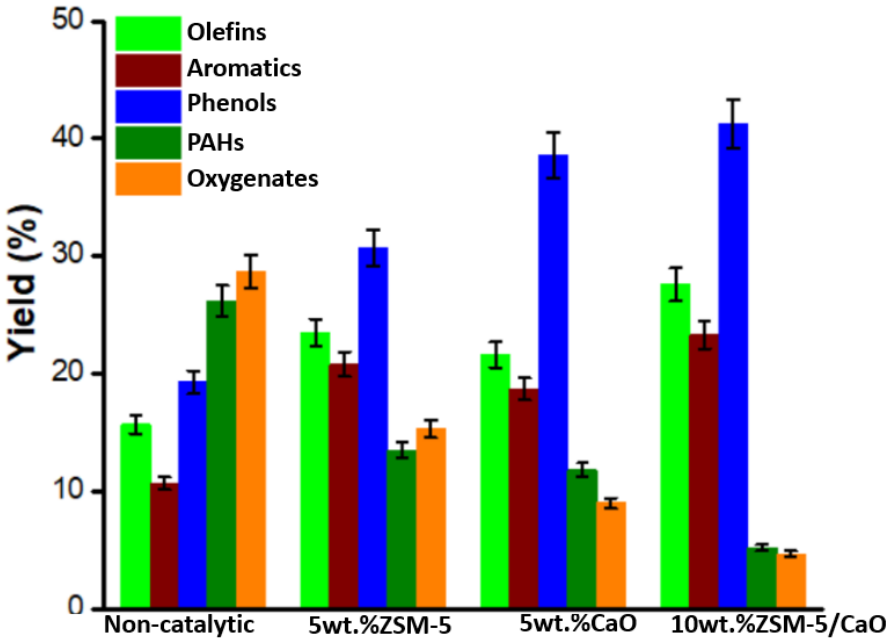

Fig. 5. Py/GC-MS analysis to examine effect of ZSM-5, CaO and ZSM-5/CaO at 500^{o}C.

The primary byproducts observed are aromatics, olefins, PAHs, phenols, and oxygenates, which make biomass an appealing source for pyrolysis. The non-catalytic pyrolysis of CW results a substantial yield of oxygenates, peaking at 28.7%. This significant proportion underscores the

306 inferior quality of the bio-oil produced. Furthermore, the presence of polycyclic aromatic
307 hydrocarbons (PAHs) at 26.2% raises critical health concerns due to their recognized carcinogenic
308 properties. Other byproducts such as olefins, aromatics, and phenols are observed at percentages
309 of 15.7%, 10.7%, and 19.3% respectively. These byproducts, while currently viewed as value-
310 added chemicals, necessitate further, both to enhance the quality of bio-oil and to mitigate the
311 health risks associated with PAHs. In line with this, we proposed catalytic pyrolysis of CW using
312 5wt.%ZSM-5, 5wt.%CaO, and 10wt.%ZSM-5/CaO. CW pyrolysis with 5wt.% ZSM-5, reveals a
313 decrease in the yield of oxygenates and PAHs to 15.3% and 13.5% respectively. Concurrently, an
314 increase in the yield of olefins, aromatics, and phenols to 23.5%, 20.8%, and 30.7% respectively
315 was observed. This phenomenon can be attributed to the conversion of light compounds, such as
316 acids, esters, and ketones, into benzene and other aromatics over ZSM-5 through cracking and
317 deoxygenation [5]. Additionally, the enhanced formation of phenols is likely due to the catalytic
318 activity of ZSM-5 for phenol formation [38]. In the case of 5wt.% CaO, the yield of oxygenates
319 and PAHs decreased to 9.1% and 11.8% respectively, while the yield of olefins, aromatics, and
320 phenols increased to 21.6%, 18.7%, and 38.6% respectively. The decreased yield of PAHs and
321 oxygenates and increased yield of phenols and aromatics can be attributed to the fact that acids,
322 esters, and ketones over CaO facilitate the formation of aromatic hydrocarbons such as phenol [5].
323 Simultaneously, CaO, as a typical cracking catalyst, can crack macromolecules in pyrolytic
324 products into micromolecules, thereby converting PAHs into aromatics and thus decreasing the
325 yield of PAHs [39]. In the instance of 10wt.% ZSM-5/CaO, there was a noted reduction in the
326 oxygenates and PAHs to 4.7% and 5.2% respectively. Concurrently, there was an increase in the
327 yield of olefins, aromatics, and phenols to 27.6%, 23.3%, and 41.3% respectively. The notable

reduction in PAHs is credited to the efficiency of CaO in inhibiting the production of naphthalenes and other polycyclic aromatics (PAHs) over ZSM-5 during the process of pyrolysis [40].

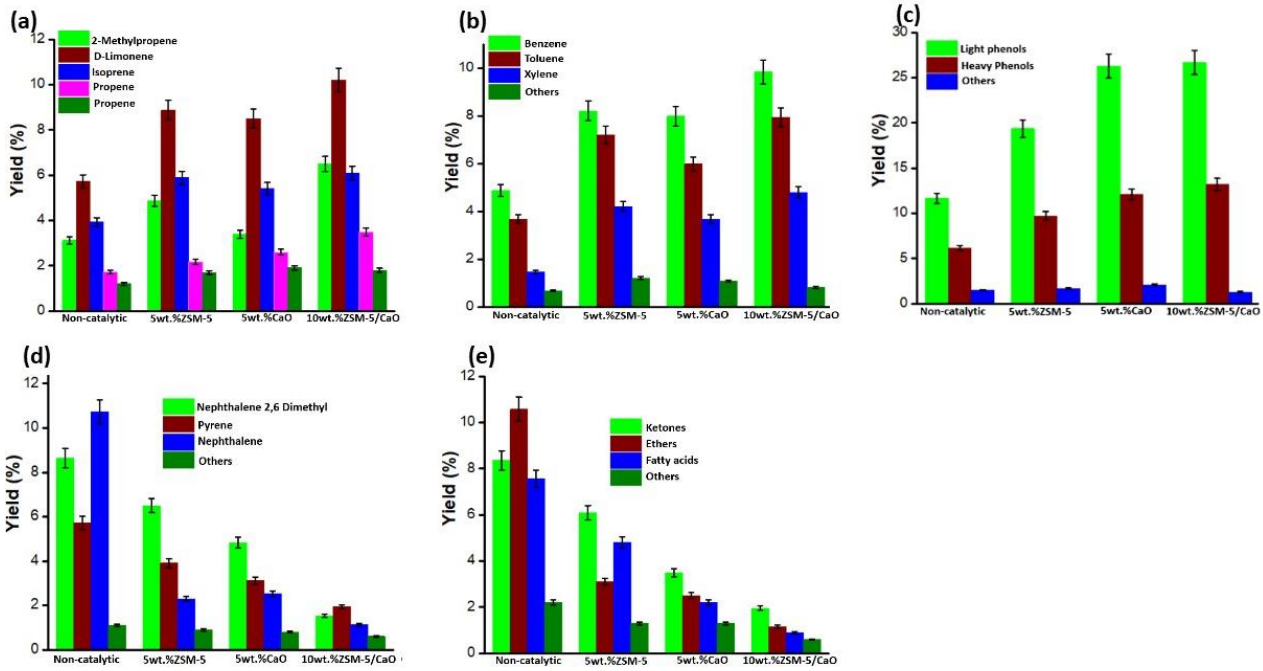

Fig. 6. Effect of 5wt.%ZSM-5, 5wt.%CaO, and 10wt.%ZSM-5/CaO during CW pyrolysis on product distribution and yield of **(a)** Olefins **(b)** Aromatics **(c)** Phenols **(d)** PAHs and **(e)** Oxygenates.

These findings confirm the synergy of ZSM and CaO in decreasing the yield of oxygenates and PAHs, while simultaneously increasing the yield of value-added chemicals such as olefins, aromatics, and phenols. For 10wt.%ZSM-5/CaO, the yield of aromatics such as benzene and toluene were found to be at its maximum at 9.8% and 7.9% respectively (Fig. 6b). Meanwhile, the yield of D-Limonene, an olefin product, was found to be highest at 10.2% (Fig. 6a). Light molecular weight phenols were found at 26.65%, which was higher than the heavier phenols found at 13.2% for 10wt.%ZSM-5/CaO (Fig. 6c). The Higher Heating Values (HHVs) for benzene and toluene are recorded at 41.8 and 40.6 MJ kg^{-1}, respectively. These values are strikingly similar to those of gasoline and diesel, which stand at 47.3 and 44.8 MJ kg^{-1}, respectively [29]. D-limonene, a compound frequently used in the chemical industry, serves as an active ingredient in various

products such as pesticides, electrical circuit boards, pigment dispersing agents, and pesticide circuit boards [41]. Thus, catalytic pyrolysis of CW with ZSM-5/CaO could potentially be a viable method to produce D-limonene, further applying it in the chemical and agricultural industries. Phenols, due to their potential applications as high-value chemicals, are deemed important. They can be used in the manufacturing of plastics among other products. An increased presence of phenols in the upgraded bio-oil could suggest a higher capacity of the respective catalyst to crack heavier compounds. Therefore, ZSM-5/CaO could serve as a promising catalyst to upgrade bio-oil with higher yield of aromatics, D-limonene and phenols.

CONCLUSION

The study on the catalytic pyrolysis of hydrogen-deficient biomass using cabbage waste demonstrates an impressive synergy of the combined ZSM-5/CaO catalyst compared to independent ZSM-5 and CaO catalyst in improving the quality of the pyrolytic products and reducing pollutants emission. With the addition of 5wt.%ZSM-5, 5wt.%CaO, and 10wt.%ZSM-5/CaO, the conversion of CW increased to 77.15%, 82.87%, 85.08% respectively from 74.08% (non-catalytic), while the residue decreased to 17.85%, 12.22%, and 9.91%, respectively from 20.91% (non-catalytic). TG-FTIR analysis showed that these catalysts reduced pollutants emission and increased value-added chemicals production by 24.96%, 28.5%, 17.39% and 75.04%, 71.5%, 82.1%, respectively compared to non-catalytic process as 34.18% and 65.82%. Moreover, relative yield of olefins, aromatics, and phenols was increased to 23.5, 21.6, 27.6% for 5wt.%ZSM-5; 20.8, 18.7, 23.3% for 5wt.%CaO; 30.7, 38.6, 41.3% for 10wt.%ZSM-5/CaO, compared to the non-catalytic process' yield of 15.7, 10.7, 19.3%. Moreover, Py/GC-MS analysis confirms that the yield of olefins, aromatics, and phenols increased to 27.6%, 23.3%, and 41.3% for 5wt.% ZSM-5; 21.6%, 18.7%, and 38.6% for 5wt.% CaO and 27.6%, 23.3%, and 41.3% for 10wt.%ZSM-5/CaO

respectively as compared to 15.7%, 10.7%, and 19.3% for non-catalytic pyrolysis Concurrently, the yield of PAH and oxygenates decreased to 13.5, 15.3% for 5wt.%ZSM-5; 11.8, 9.1% for 5wt.%CaO; 5.2, 4.7% for 10wt.%ZSM-5/CaO, in contrast to the non-catalytic process' 26.2, 28.7%. Ultimately, these results demonstrate the synergistic effect of ZSM-5/CaO in enhancing biomass conversion, reducing residue formation, promoting value-added chemicals production and reducing pollutants emission and, thereby establishing it an ideal catalyst for biomass pyrolysis. On one side, these findings support using ZSM-5/CaO as an effective catalyst in hydrogen-deficient biomass pyrolysis, advancing sustainable waste management and biofuel production technologies. On other side, during catalyst pyrolysis, coke formation covers active sites and blocks pores, leading to catalyst deactivation which is a significant challenge to the technology's industrial application. To overcome this, incorporating promoters like Fe, Cu, Co, and Ce, which have abundant oxygen vacancies or suitable redox potential, is advantageous. These promoters facilitate the reaction of oxygen species with carbon deposits on the catalyst, preventing coke accumulation and thus enhancing both stability and activity, ultimately improving process efficiency.

Appendix A

A1. Nomenclature Table

	Abbreviations
Cabbage waste	CW
Hydrogen-deficient biomass	H-DB
Thermogravimetric analysis	TGA
Differential thermogravimetric analysis	DTG
Thermogravimetric-fourier transform infrared spectroscopy	TG-FTIR
Pyrolysis–gas chromatography–mass spectrometry	Py/GC-MS
Zeolite socony mobil–5	ZSM-5
Calcium oxide	CaO
Higher heating value	HHV
polycyclic aromatic hydrocarbon	PAH

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SUPPORTING INFORMATIONS

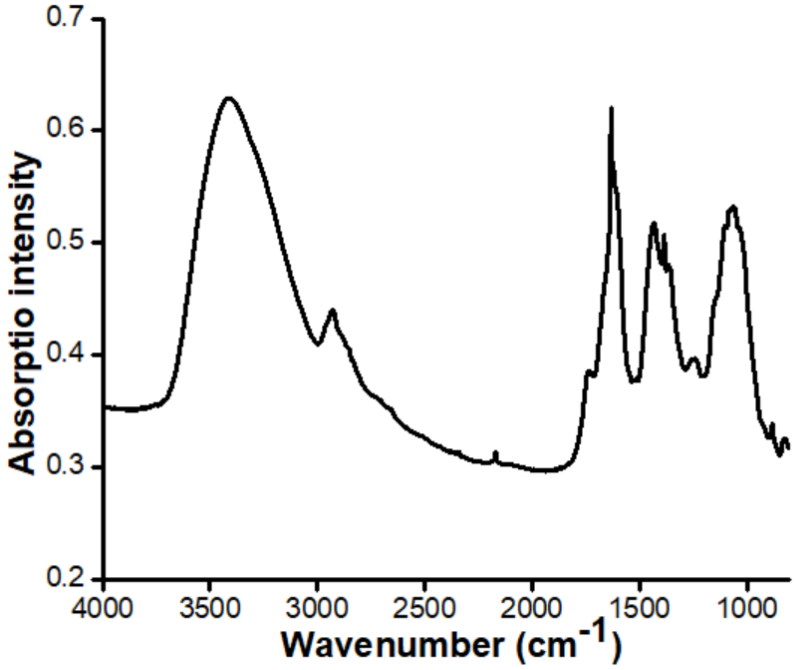


Fig. S1. FTIR analysis of as-received CW

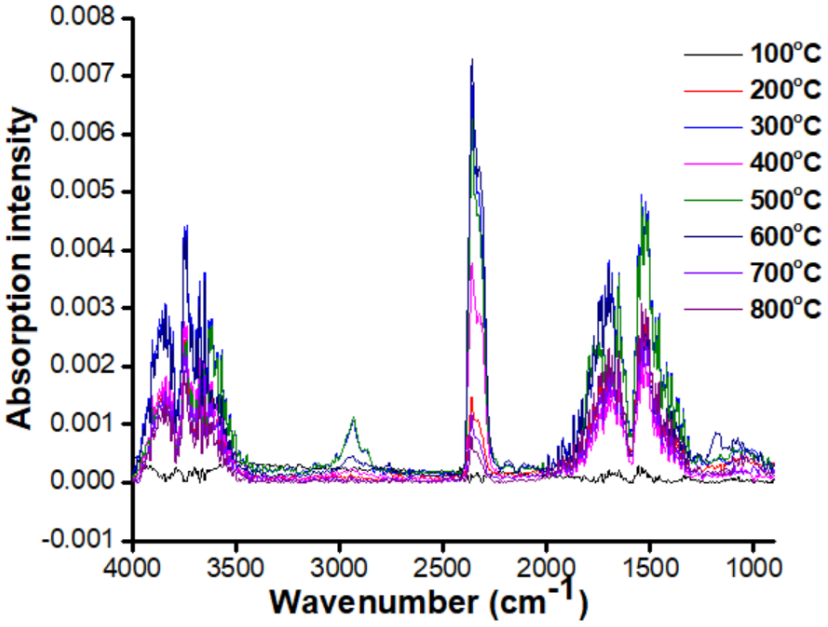
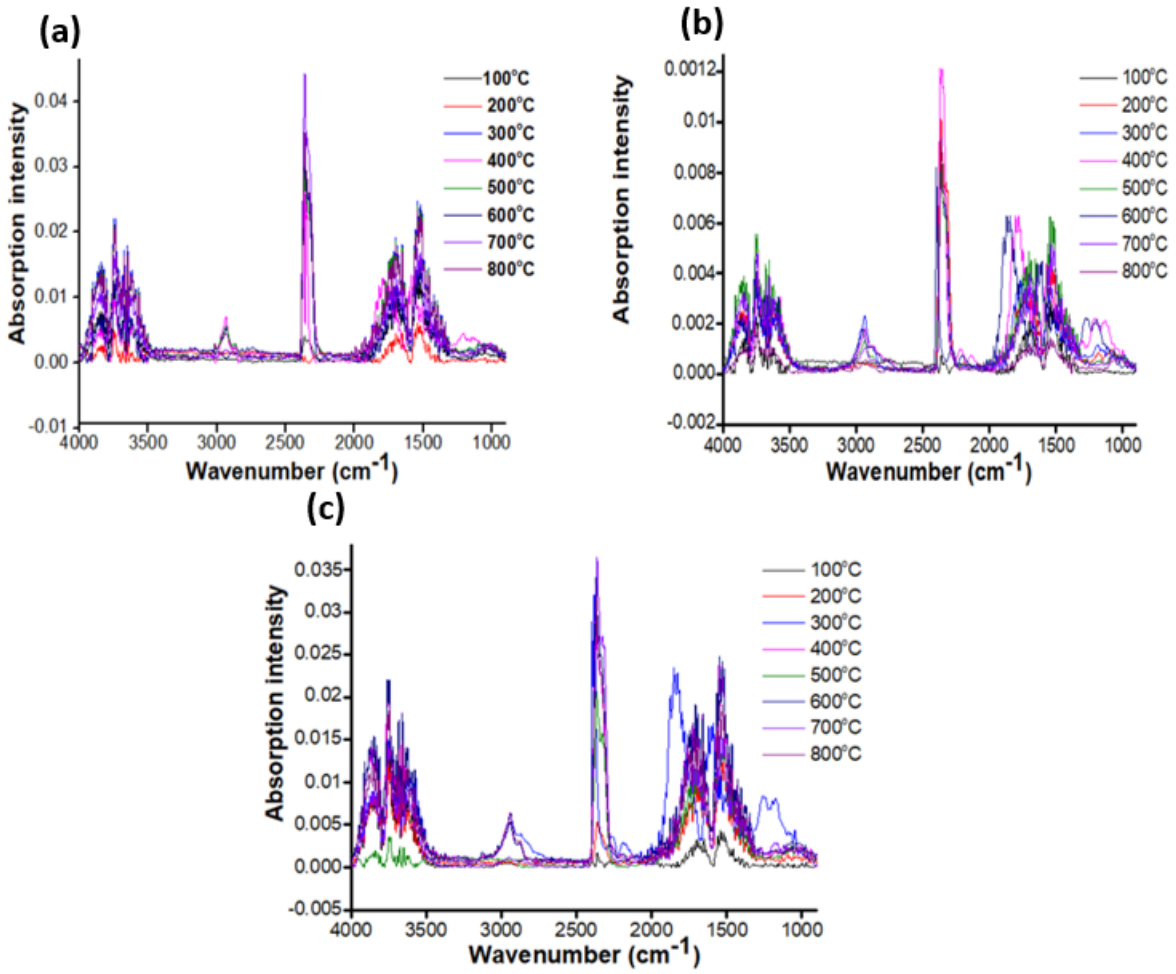
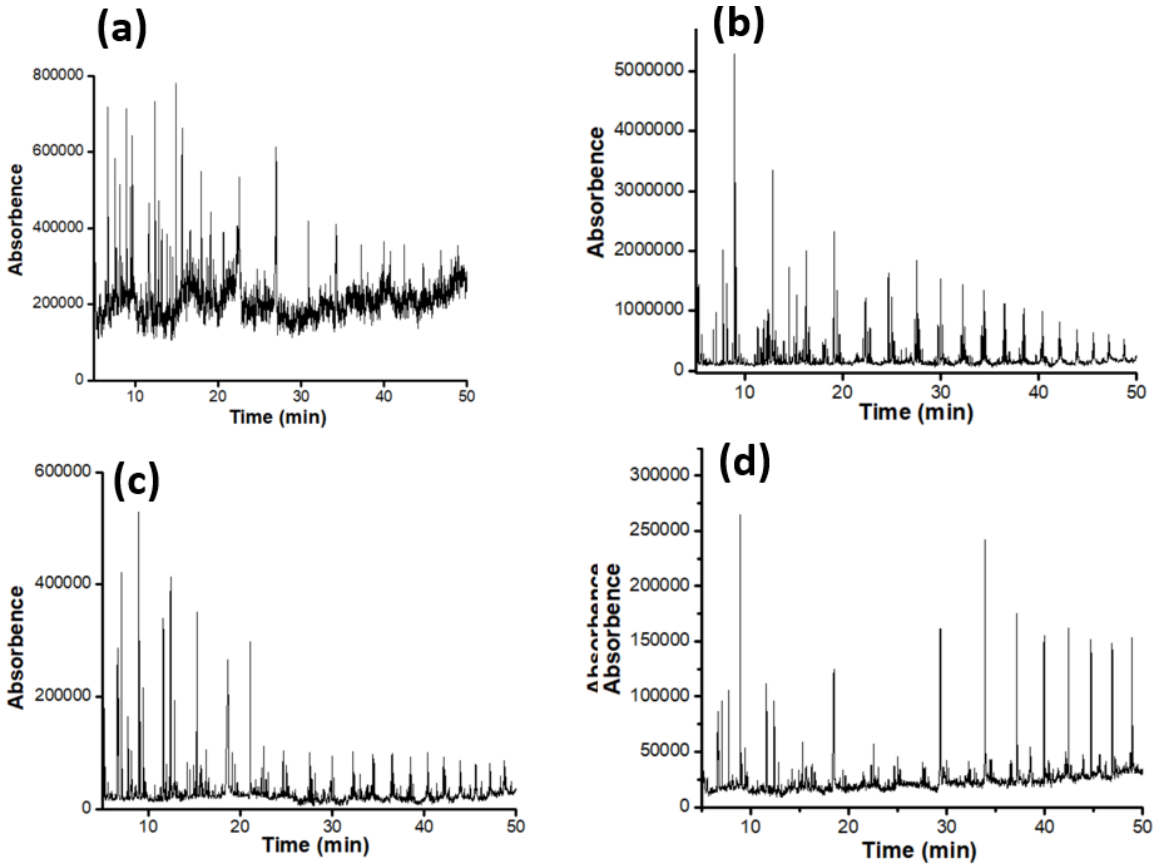


Fig. S2. FTIR spectra of evolved gaseous products during non-catalytic pyrolysis of CW.



557

558 **Fig. S3.** FTIR spectra during CW pyrolysis with **(a)** 5wt.%ZSM-5, **(b)** 5wt.%CaO, and **(c)**
559 10wt.%ZSM-5/CaO.



560

561 **Fig. S4.** GCMS analysis for **(a)** non-catalytic, **(b)** 5wt.% ZSM-5, **(c)** 5wt.% CaO and **(d)** 10 wt.%
562 ZSM5-/C