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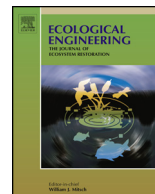
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# A comparison of catalysts zeolite and calcined dolomite for gas production from pyrolysis of municipal solid waste (MSW)



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## ABSTRACT

Gas production and analysis from pyrolysis of municipal solid waste (MSW) with zeolite and calcined dolomite as catalyst has been investigated in a downstream fixed-bed reactor over the temperature range of 200–750 °C. Gas production from pyrolysis of MSW varied in the range of 49–57 mol%. The results indicated the presence of calcined dolomite influenced significantly the product yields and gas composition in pyrolysis process, and revealed essential catalytic performance on increasing gas yield and decreasing oil yield and char yield comparing to zeolite and non-catalytic process. A higher temperature 600–750 °C resulted in a higher conversion of MSW into gas production with a greatly increasing of CO contents. Consequently, CO is a key factor to produce renewable energy and bio-gases (syngas and methane).

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## 1. Introduction

Municipal solid waste (MSW) is primarily waste which is produced by the household, but also includes some commercial and industrial waste that is similar in nature to household waste and has been deposited in municipal landfill sites. MSW can be a liability if requiring disposal but also represents a considerable resource that can be beneficially recovered, e.g., by the recycling of materials such as aluminum cans, metals, glass, fibers, etc., or through recovery operations such as conversion to energy and composting. However, significant quantities of MSW continue to be disposed of in landfill largely due to its low cost and ready availability. Clearly, new waste management practices are needed.

In landfill the biodegradable components of MSW (e.g., paper and food wastes) decompose and emit methane – a greenhouse gas 23 times more potent than carbon dioxide and the cause of significant environmental problems. Other components (e.g., leachate) can also cause significant environmental pollution in air and ground water and give rise to odor. In general, valuable resources are wasted (Sakai et al., 1996).

For these reasons most countries aim to reduce their dependence on the use of landfills for MSW.

Recycling municipal waste can be done in several ways, including some alternative ways that have less of a harmful impact on the environment. Environmental recycle advocates point out that the old methods of taking care of municipal waste disposal are not effective, and cause great harm to the environment. Landfills have a large harmful environmental impact, in the form of leachate which can contain harmful metals and chemical pollutants, and this can get into the groundwater. Landfills also accumulate greenhouse gases, from the decomposition process, which contribute to global warming. There are other alternative methods of municipal waste disposal that can be more eco friendly, and some can be used for conversion to energy source. Recycling municipal waste can be a source of energy for our home and transport.

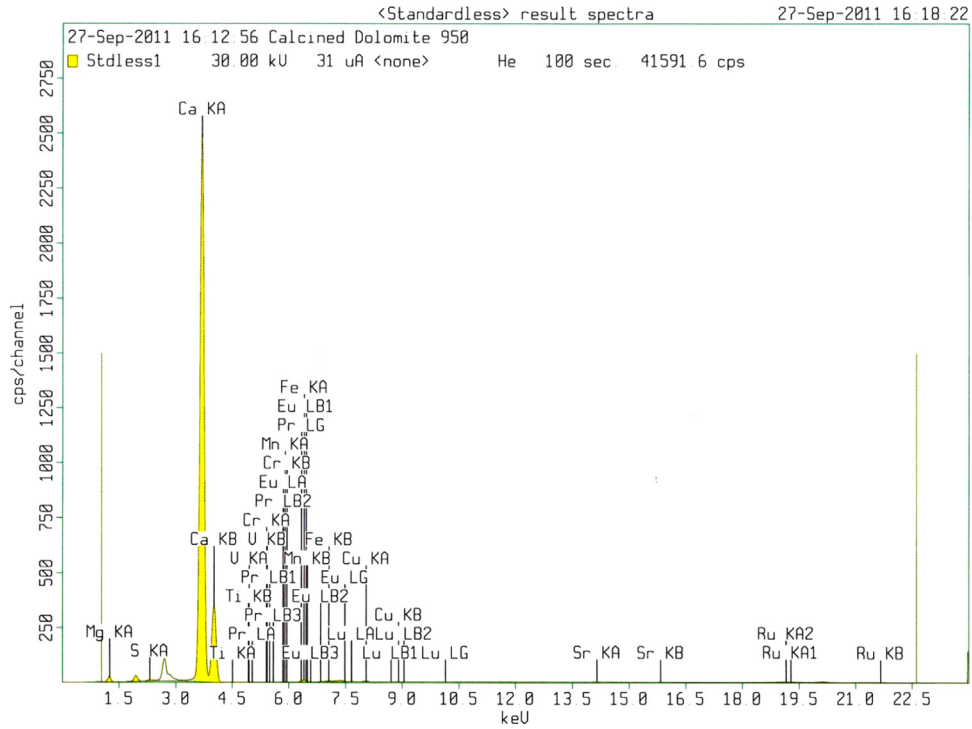
Nonetheless, different waste treatment, management and disposal methods have been applied besides the traditional methods of incineration and landfilling. Nowadays massive attentions are being paid to energy efficient, environmentally friendly and economically effective technologies of pyrolysis processing of waste. MSW pyrolysis is apparently very to reduce and avoid corrosion and emissions by refraining alkali and heavy metals (except cadmium and mercury), chlorine and sulfur within the process residues, prevent PCDD/F formation and reduce thermal NO<sub>x</sub> formation because of the lower temperatures and diminishing conditions. Application of pyrolysis technology to MSW can avoid these problems and it is one of the promising technologies for waste-to-energy (WTE) application.

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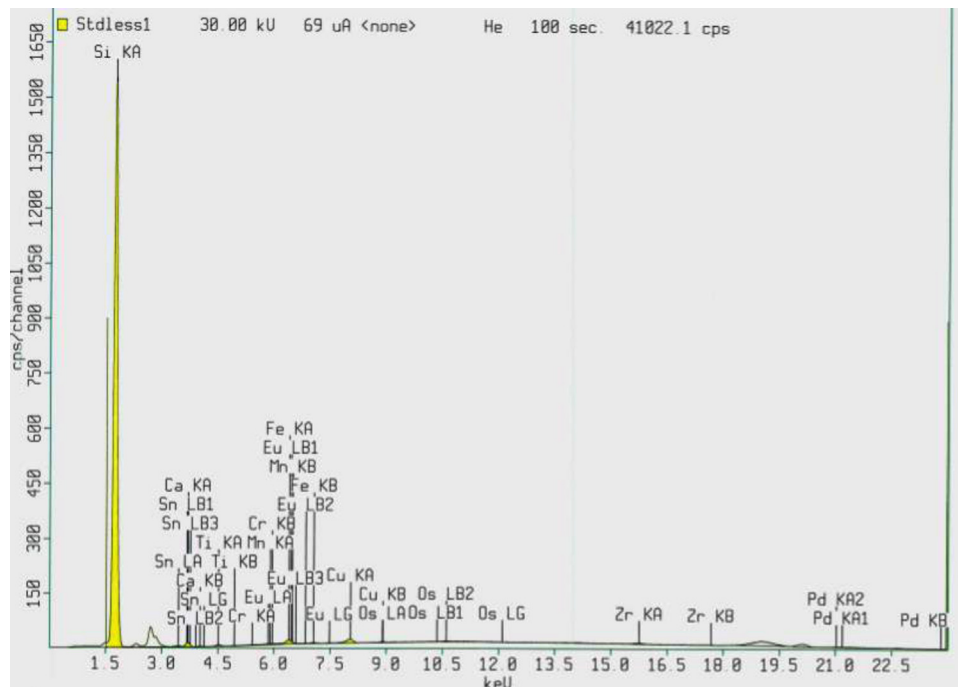


**Table 2**  
X-ray analysis of zeolite.

Compound	SiO <sub>2</sub>	CaO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	CuO	ZrO <sub>2</sub>	PdO	SnO	Eu <sub>2</sub> O <sub>3</sub>	OsO <sub>2</sub>
Conc	98.38	0.39	0.10	0.024	0.003	0.094	0.069	0.030	0.17	0.60	0.11	0.027
Unit	%	%	%	%	%	%	%	%	%	%	%	%



**Fig. 1.** X-ray patterns of the calcined dolomite.



**Fig. 2.** X-ray patterns of zeolite.

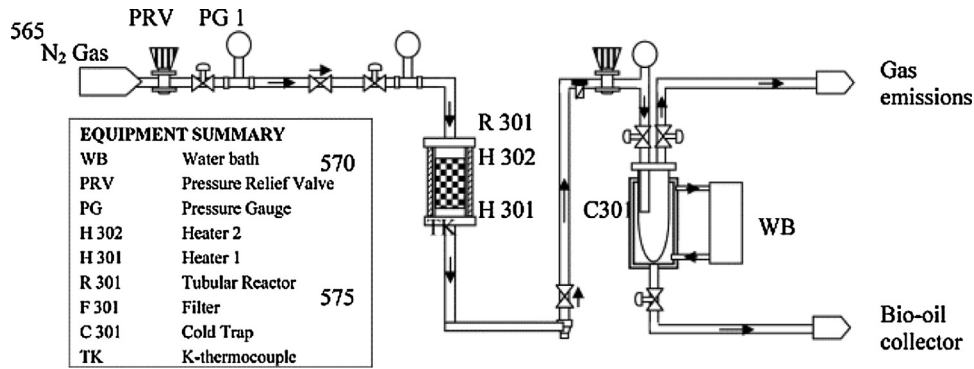


Fig. 3. Schematic diagram of the fix-bed reactor.

tube reactor was electrically heated with 10 °C/min to reaction temperature. In this study, the reaction temperature was controlled from 200 to 750 °C in 50 °C increments (heating rate h/r), and the operating pressure in the reactor was close to the atmospheric pressure. Prior to each test, catalyst were held in the stainless tube, and then a porous ceramic of 80 mm in diameter and 10 mm in thickness was placed on the catalyst for collecting the char from MSW pyrolysis and uniform distribution of gas through the catalyst bed.

The procedure for a typical catalytic pyrolysis experiment is described below. Prior to each experiment, calcined dolomite was held in the stainless tube. Each run was performed with the same quantity of representative sample of MSW. The shredded MSW feedstock was loaded in a hopper. The solid char residue was mostly collected on the porous ceramic, the produced gas and fine particles passed through the cyclone and fiber wool filter, thus the fine particles were removed. The condensable matter was quenched as the gas passed through the water condenser. Subsequently, the product gas was investigated by using gas analyzer. At last heating of the furnace stopped, and the reactor was cooled to the ambient temperature.

After each experiment, the char residues collected on the porous ceramic inside the tube and in the cyclone were weighed to determine the amount unconverted solid char. The weight of liquid produced in the condenser was weighed and recorded. In general, it took 25 min for the experiment to reach a stable state, to ensure the reliability of test data, each experiment was repeated several times, and the results were in good agreement.

#### 2.4. Method of gas analysis

In this research investigation, the Gas Analyzer “Pocket Gas” (br. name: Applus) was used to identify the gas composition from pyrolysis process. Gas Analyzer Pocket Gas uses NDIR measurement method. This method measures HC, CO and CO<sub>2</sub> components in the sample, non-scanning infrared light frequencies to characterize the gas concentrations. NDIR absorption profiles are the basis for measurement. The concentration of a gas volume is a function of the quantity of gas molecules in the sample. The absorption of infrared light increases with the number of gas molecules in the light path. As the concentration of infrared-absorbing gas increases, the transmission of infrared light decreases. A basic NDIR methodological measurement system has been applied for pyrolysis process. Gas analyzer measurement ranges were shown in Table 3.

The specification of gas analyzer:

Temperature: 0–50 °C oper., –20 to 70 °C storage  
 Humidity: Up to 95% non-considering  
 Altitude: –300 to 2500 m

Table 3  
 Gas analyzer measurement ranges.

Gas yield	Range	Resolution
HC	0–2000 ppm	1 ppm
CO	0–15%	0.001 vol%
CO <sub>2</sub>	0–20%	0.01 vol%
O <sub>2</sub>	0–25%	0.01 vol%
NOx	0–5000 ppm	1 ppm

Vibration: 1.5 G sinusoidal 5–1000 Hz  
 Shock: 1.22 m drop to concentrate floor (gas analyzer)  
 Response time: 0–90% ← 8 s for NDIR measurements  
 Pocket PC  
 Power: 5 VDC 2 Amps max  
 Operating system: Windows Mobile/CE version 3.0 or later.

### 3. Results and discussion

#### 3.1. MSW sampling. Proximate and ultimate analysis of MSW sample

MSW sampling characterization was investigated for a period of two month. Obtained result from sorting process and quantity of each individual component of the MSW at Padang Siding landfill shows in Fig. 4.

As Fig. 4 indicates MSW such as, wood and kitchen garbage waste followed by plastic bag and solid plastic make up the largest fraction of generated waste in Padang Siding landfill. Top seven individual materials were most prevalent in the Padang Siding disposed waste stream included of wood waste (37.58%), kitchen garbage (16.32%), plastic bag (15.27%), solid plastic (14.57%), textile (9.63%), glass (4.20%) and ferrous materials (2.42%). The high percentage of wood waste can be explained by increasing the demand

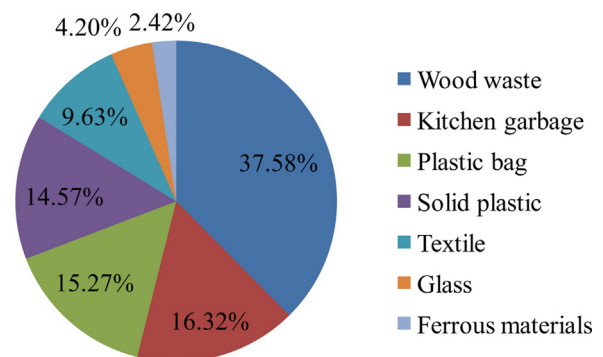


Fig. 4. Municipal solid waste (MSW) composition.

**Table 4**  
Proximate and ultimate analysis of MSW.

Proximate analysis		Ultimate analysis	
Composition	Weight (%)	Composition	Weight (%)
Moisture	16.9	C (carbon)	53.84
Volatile	55.1	H (hydrogen)	5.73
Fixed carbon	8	O (oxygen)	32.93
Ash	20	N (nitrogen)	1.68
Calorific value, kcal/kg	2388	S (sulfur)	0.87

on wood by households to use in a different area of building and for daily use as well. In addition, a few factories are located in Perlis, for instance “Sugar Factory”, the waste materials from these factories mostly include of high volume of wood, different type of plastic which are mixed with small amount of glass and ferrous materials.

Proximate analysis involves determination of moisture content, volatile matter, ash content, fixed carbon and also calorific value of composite sample. The analysis was according to ASTM method and ultimate analysis demonstrates determination of chemical characteristics of MSW sample. Results from proximate and ultimate analysis were shown in Table 4.

Table 4 shows that the proximate and ultimate analysis of MSW used in this research. The table shows moisture content (16.9 wt%) and fixed carbon (8 wt%). The moisture content is measured with the amount of water lost from materials upon drying to a constant weight. It is directly affected by chemical and physical properties of material which enable it to absorb the exiting water in the environment. Fixed carbon is the carbon remaining on surface as charcoal. In addition, Table 4 highlights processed MSW has volatile matter content (55.1 wt%) and ash content (20 wt%); both parameters have influence on the pyrolysis characteristics. The MSW is easier to ignite and to gasify than coal apparently due its volatile matter although the pyrolysis is expected to be more rapid and difficult to control. The calorific value (heating value) of MSW was obtained to be 2388 kcal/kg based on the bomb calorimeter test. The results of ultimate analysis that was investigated by CHNS/O (Perkin Elmer), elemental analyzer was also shown in Table 4.

### 3.2. Mechanism of catalytic pyrolysis of MSW

According to the literatures (Blasi, 2008; Li et al., 2007), the catalytic pyrolysis process of MSW can be divided into two steps:

Primary pyrolysis termed MSW decomposition. This step is a thermochemical decomposition of MSW with production of water, tar, char and volatiles. In this process, temperature was the most important parameter influencing the product yields distribution. This step could perform at a lower temperature  $\sim 300^\circ\text{C}$ , and last until a temperature of  $700^\circ\text{C}$  or even higher. As the pyrolysis temperature increases, the moisture inside the MSW particles evaporated first, then thermal degradation and devolatilization of dried portion of the particles took place, and the volatile species gradually evolved out from the particles surface and underwent further pyrolysis.

Then, the second step secondary reactions of tar cracking occur at higher temperatures ( $>400^\circ\text{C}$ ). The main secondary reactions of tar cracking and shifting include decarboxylation, decarbonylation,

dehydrogenation, cyclization, aromatization, and polymerizing reactions, which were given in order of increasing pyrolysis severity (e.g., increasing temperature). Part of vapors (mainly heavy oil fraction) were absorbed by the active surface of the catalyst, and then cracked to light vapors. The light vapors then underwent series reactions such as deoxygenation, cracking to form  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ , alkanes, alkenes and aromatic hydrocarbons. These reactions would result in a decrease of tar vapors and increase of gas and water yields. When all of the volatile species were removed from the solid, a residue of char was left.

According to above mentioned literatures, temperature and the presence of catalysts are among the most important parameters that influenced the product yield from this process. Studies had also found that maximum pyrolytic oil can be obtained in the temperature range of  $400$  and  $550^\circ\text{C}$ . Due to the secondary reactions, the pyrolytic oil yield decreased parallel with gas amount increasing as temperature operated over  $500^\circ\text{C}$ .

### 3.3. Catalysts activity

#### 3.3.1. Product yields

The MSW pyrolysis experiments at the reactor temperature of  $750^\circ\text{C}$  with zeolite and calcined dolomite were carried out to study the influence of the catalysts on product yields, the product yields (gas, oil and char) from pyrolysis process were presented in Table 5. As illustrated in Table 5, there was a remarkable increase in gas yield from 24.98 wt% with zeolite to 56.67 wt% with calcined dolomite. The oil yield decreased significantly from 36.35 wt% with zeolite to 10.88 wt% with calcined dolomite. It was because that the low oil yield resulted from oxygen removal to water,  $\text{CO}_2$  and  $\text{CO}$ , from coke formation on the catalysts and from a significant increase in gas yield due to catalysis (Tsai et al., 2007; Vitolo et al., 1999). The char yield resulted 38.66 wt% with zeolite and 32.44 wt% with calcined dolomite, the similar tendency was found by Williams and Horne (1994, 1995), who pyrolyzed biomass in the form of wood in a fluidized bed and upgraded vapors with catalysts in a fixed bed downstream. Furthermore, the details of the materials balance calculation at different reactor temperatures over the range of  $200$ – $750^\circ\text{C}$  were presented in Table 5. The overall material balance had a closure of  $\sim 99.99\%$ .

Thus, pyrolysis product yields profile confirmed that the catalysts promote depolymerization processes to yield a strong decomposition (low solid yield) or a strong liquid phase cracking (low liquid yield), and hence a higher hydrogen formation, since this gas was formed from liquid cracking (Encinar et al., 1997).

#### 3.3.2. Gas composition

The gas composition with zeolite, calcined dolomite and also non-catalytic pyrolysis at the reactor temperature of  $200$ – $750^\circ\text{C}$  were presented in Figs. 5, 6 and 7, respectively. It indicated that the gas components were  $\text{HC}$ ,  $\text{CO}$  and  $\text{CO}_2$ . In the presence of calcined dolomite  $\text{CO}$  contents increased significantly, while  $\text{HC}$ ,  $\text{CO}_2$  contents showed the opposite tendencies. Total percentages of product gas were 24.98% (catalytic pyrolysis with zeolite), 39.91% (non-catalytic pyrolysis) and 56.67% (catalytic pyrolysis with calcined dolomite). Furthermore, a remarkable decrease of  $\text{CO}_2$

**Table 5**  
Product yields and recovery from catalytic (calcined dolomite and zeolite) pyrolysis of MSW at  $200$ – $750^\circ\text{C}$  reactor temperature.

Type of MSW pyrolysis	Gas (wt%)	Oil (wt%)	Char (wt%)	Recovery (wt%)
Catalytic (calcined dolomite)	56.67	10.88	32.44	99.99
Catalytic (zeolite)	24.98	36.35	38.66	99.99
Non-catalytic	39.91	21.72	38.36	99.99

Recovery (wt%) = Gas (wt%) + Oil (wt%) + Char (wt%).

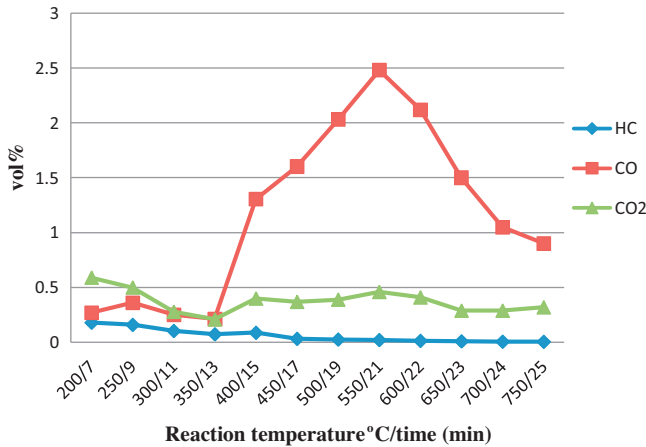


Fig. 5. Gas concentrations versus of catalyst calcined dolomite at the reaction temperature 200–750 °C and time 7–25 (min).

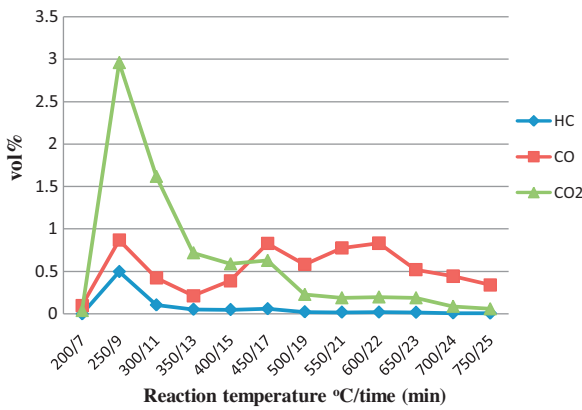


Fig. 6. The gas concentrations with catalyst zeolite at the reaction temperature 200–750 °C and time 7–25 (min).

content was achieved. In the presence of calcined dolomite, the formation rate of gaseous products, especially CO increased compared to zeolite. It was concluded that calcined dolomite is an effective to the conversion of MSW to useful gas production. Consequently, comparison of the gas, char and oil yield components of catalytic pyrolysis with zeolite and calcined dolomite, as well as non-catalytic pyrolysis were emphasized in Fig. 8.

Table 6  
Catalytic calcined dolomite and zeolite influence of reactor temperature on product concentration and gas characterization.

Gas concentration	Temperature °C											
	200	250	300	350	400	450	500	550	600	650	700	750
<i>Catalytic calcined dolomite influence of reactor temperature on product concentrations and gas characterization</i>												
HC vol%	0.004	0.18	0.16	0.1041	0.0735	0.0872	0.0032	0.0252	0.0207	0.0133	0.0055	0.0034
CO vol%	0.02	0.27	0.360	0.253	0.214	1.305	1.602	2.030	2.480	2.119	1.05	0.901
CO <sub>2</sub> vol%	0.08	0.59	0.50	0.28	0.21	0.40	0.37	0.39	0.46	0.41	0.29	0.32
<i>Catalytic zeolite influence of reactor temperature on product concentrations and gas characterization</i>												
HC vol%	0	0.4977	0.1046	0.0533	0.0504	0.06	0.024	0.0198	0.0202	0.018	0.0106	0.0083
CO vol%	0.01	0.866	0.424	0.215	0.391	0.83	0.583	0.776	0.831	0.52	0.444	0.341
CO <sub>2</sub> vol%	0.04	2.96	1.62	0.72	0.59	0.63	0.23	0.19	0.2	0.19	0.09	0.06
<i>Non-catalytic influence of reactor temperature on product concentrations and gas characterization</i>												
HC vol%	0.0002	0.0015	0.1145	0.0655	0.0378	0.0491	0.0396	0.02	0.0148	0.0101	0.0043	0.0033
CO vol%	0	0.055	0.588	0.324	0.191	1.071	1.365	1.256	1.018	0.848	0.315	0.255
CO <sub>2</sub> vol%	0.01	0.73	2.04	0.97	0.51	0.55	0.35	0.26	0.19	0.11	0.02	0

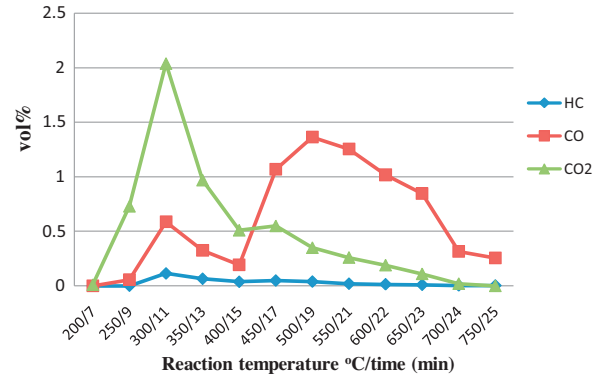


Fig. 7. The gas concentrations of non-catalytic pyrolysis at the reaction temperature 200–750 °C and time 7–25 (min).

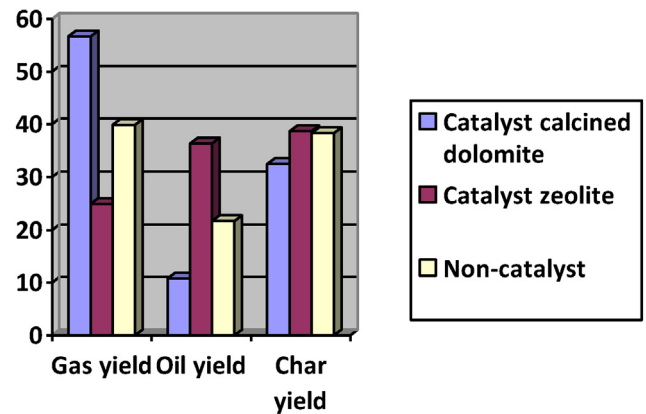


Fig. 8. Comparison of the overall gas, char and oil yield components of catalytic (calcined dolomite; zeolite) and non-catalytic pyrolysis.

### 3.4. Influence of temperature

The pyrolysis process is endothermic strengthened by increasing temperature. Therefore, the reactor temperature had a significant influence on pyrolysis process. As shown in Table 6, higher temperatures would favor tar decomposition and the thermal cracking of gases to increase the proportion of CO gas significantly. Thus, as the reactor temperature increased, the gas yield sharply increased, while the oil and char yields decreased, the similar tendencies were found by Williams and Horne (1994, 1995). It was because that the reactor temperature influenced the heating

rate and the pyrolysis process, which determined products distribution (Encinar et al., 1996; Scott et al., 1988). Volatiles are more sufficiently released from MSW particles as the reactor temperature increased. The extent of secondary reactions is affected by reactor temperature. At the higher temperature (>500 °C), the main occurring secondary reactions, such as the cracking of cyclanes and the breaking of the long chains of macromolecules, the reaction rate of which increases with the increase of the temperature, result in an increase of the gas yields and a decrease of the tar production at the higher temperature (Fagbemi et al., 2001; Wei et al., 2006).

#### 4. Conclusion

The pyrolysis of MSW with catalysts zeolite and calcined dolomite for gas analysis was performed at atmospheric pressure in a fixed-bed reactor under the same conditions. The calcined dolomite and zeolite has been used under high temperature. The data showed that the presence of calcined dolomite influenced significantly the product yields and gas composition in pyrolysis process. Calcined dolomite revealed significant catalytic performance on increasing gas yield and decreasing oil yield and char yield compared to catalytic zeolite process.

Reactor temperature also played a great role on the product yields and gas composition with calcined dolomite. A higher temperature resulted in a higher conversion of MSW into product gas of CO contents. Meanwhile, CO is a main gas product and link for renewable energy. With temperature increasing from 500 to 750 °C, the yield of char and tar decreased while dry gas yield increased.

The results indicated that there is a strong potential for producing renewable gas from MSW by a simple pyrolysis process with inexpensive and abundant dolomite as catalysts. Moreover, this

paper aims to convert MSW which are essentially waste materials to useful and valuable gas product.

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