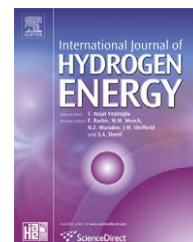


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Hydrogen-rich gas from catalytic steam gasification of municipal solid waste (MSW): Influence of steam to MSW ratios and weight hourly space velocity on gas production and composition

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ARTICLE INFO

Article history:

Received 30 September 2008

Received in revised form

14 November 2008

Accepted 14 November 2008

Published online ■

Keywords:

Hydrogen

Municipal solid waste

Steam gasification

Dolomite

Catalyst

Weight hourly space velocity

Thermodynamic equilibrium

Kinetic model

ABSTRACT

The present work deals with a study coupling experiments and modeling of catalytic steam gasification of municipal solid waste (MSW) for producing hydrogen-rich gas or syngas ($H_2 + CO$) with calcined dolomite as a catalyst in a bench-scale downstream fixed bed reactor. The influence of steam to MSW ratios (S/M) on gas production and composition was studied at 900 °C over the S/M range of 0.39–1.04, for weight hourly space velocity (WHSV) in the range of 1.22–1.51 h^{-1} . Over the ranges of experimental conditions examined, calcined dolomite revealed better catalytic performance at the presence of steam. H_2 and CO_2 contents increased with S/M increasing, while CO and CH_4 contents decreased sharply, the contents of CH_4 , C_2H_4 and C_2H_6 were relatively small, and the influence of S/M was insignificant. The highest H_2 content of 53.22 mol %, the highest H_2 yield of 42.98 mol H_2 /kg MSW, and the highest H_2 potential yield of 59.83 mol H_2 /kg MSW were achieved at the highest S/M level of 1.04. Furthermore, there was a good agreement between the experimental gas composition and that corresponding to thermodynamic equilibrium data calculated using GasEq model. Consequently, a kinetic model was proposed for describing the variation of H_2 yield and carbon conversion efficiency with S/M during the catalytic steam gasification of MSW. The kinetic model revealed a good performance between experimental results and the kinetic model.

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1. Introduction

The amount of municipal solid wastes (MSWs) is increasing dramatically in the world. Yields of MSW reach approximately 900 million tonnes in the world each year, while over 200 million tonnes in China. Recently, MSW increased at an annual rate of 8–10%, and it reached 150×10^6 tonnes in 2004

[1]. In addition, the disposal of MSW has become a critical and costly problem. The traditional landfilling method requires large amounts of land and contaminates air, water and soil [2]. Furthermore, incineration has drawbacks as well particularly harmful emissions of acidic gases (SO_x , HCl, NO_x , etc.), dioxin and leachable toxic heavy metals [3]. Dioxin is a very toxic chemical that can bind to a hormone receptor and cause

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a serious problem to the body. Carcinogenicity and mutagenicity are the most notorious effects of dioxin. Dioxin involves polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (PCBs) [4]. At the same time, several environmental disasters have increased the sensitivity of world-wide public opinion towards the effect that environmental pollution has on human health and climate change. Thus more and more attentions are being paid to energy efficient, environment friendly and economically sound technologies of gasification process of waste that could contribute to transformation in the management of MSW. Improved energy extraction and pollution control would make it more attractive than conventional waste treatment, typically dominated by incineration or landfilling [5]. Gasification process has been applied in recent years for the purpose of energy recovery in WTE (waste to energy) plants. There have been many reports on the production of clean gas from the gasification of solids [6–9] such as hydrogen-rich gas or syngas. Hydrogen production from renewable sources has been identified as a key step towards a sustainable hydrogen economy.

Presently, hydrogen is produced mainly by catalytic steam reforming of natural gas. However, in order to have environment friendly hydrogen, it must be produced from renewable resources [10], several studies on the gasification of MSW have already been investigated [11–16]. The catalytic steam gasification of MSW has been considered to be a promising method for future energy systems to meet environmental requirements, and provides one of the most cost-competitive means of obtaining hydrogen-rich gas or syngas from renewable resources, which are used as feedstock for producing hydrogen for methanol [17] and ammonia synthesis or for fuel cell applications and hydrogen combustion engines to release its stored energy [18,19]. Hydrogen-rich gas can also be converted to liquid transportation fuels using Fischer–Tropsch synthesis [20].

In order to develop an efficient and economically competitive clean MSW gasification process, it is necessary to understand the mechanism and kinetics of MSW, which can provide valuable information for proper design and operation of gasifiers. But very few reports involve catalytic steam gasification of MSW into hydrogen-rich gas or syngas ($H_2 + CO$). In the present work, the organic fractions of MSW as an energy resource by catalytic gasification process with steam was investigated in a lab-scale continuously feeding fixed bed reactor, this study aims to determine the influence of S/M and WHSV on gas production and composition, and to compare the experimental gas composition with that corresponding to thermodynamic equilibrium data calculated using GasEq model. Furthermore, a kinetic model was proposed for describing the variation of carbon conversion efficiency and H_2 yield with S/M during the catalytic steam gasification of MSW.

2. Experimental section

2.1. MSW samples

The MSW samples were collected from waste dumpsites at Huazhong University of Science and Technology (HUST),

Wuhan, China. The MSW samples were dried under the sun for a period of 7 days to reduce the moisture content. The moisture content of the MSW samples was 8.80%. Components representing the major part of the organic fraction have been studied. MSW samples were a mixture of five different components of kitchen garbage, paper, textile, wood, and plastic. Percent of different components is listed in Table 1. The organic fraction of the MSW samples were first dried at 105 °C for 4 h, then shredded into particles in sizes of approximately 5 mm, and mixed before performing the experiments to ensure representative MSW samples from the different materials. The results of ultimate and proximate analyses of MSW samples are listed in Table 2.

2.2. Catalyst

The tar formed during gasification is one of the major issues, catalytic pyrolysis or gasification for tar reduction has been extensively reported in the literatures [21–23]. The use of dolomite as a catalyst in biomass gasification had attracted much attention, because it is inexpensive and abundant and can significantly reduce the tar content of the product gas from a reactor, but they are significantly active only above 800 °C [24]. Similarly, during MSW gasification process tar was formed, calcined dolomite was used to eliminate tar. Natural dolomite was ground and sieved, the particle with a size of 3–10 mm was calcined in muffle oven (Jinhui, Zhejiang) at 900 °C for 4 h. Calcined dolomite was used as a catalyst in this study. The surface characteristics and XRD patterns of natural and calcined dolomite are listed in Table 3 and Fig. 1, respectively.

2.3. Apparatus and procedures

A process flow diagram of catalytic steam gasification process is shown schematically in Fig. 2. In this process, MSW catalytic gasification was conducted on a bench-scale fixed bed reactor using calcined dolomite as a catalyst. The MSW sample was loaded in a feedstock hopper with a maximum capacity of 2 L, which was fitted with an air-tight closure system; during the experiments, the material was continuously fed into the reactor by means of a continuous screw-driver device, whose rotation was ruled by an inverter. The catalytic gasification system consists essentially of a 0Cr25Ni20 stainless tube (i.d. 81 mm, o.d. 89 mm, height 1400 mm), a gas cleaning section containing a cyclone solid collector and a fiber wool filter, a cooling system for the separation of water and condensable organic vapors (tar), and various gas measurement devices. The stainless tube reactor was electrically heated with 10 °C/min to reaction temperature. In this study, the reaction temperature was controlled at 900 °C, and the operating pressure in the reactor was close to the atmospheric pressure. Prior to each test, catalyst was held in the stainless tube, and then a porous ceramic of 80 mm in diameter and 10 mm in

Table 1 – Components in MSW samples (wt %).

Kitchen garbage	Paper	Textile	Wood	Plastic
68.96	9.95	2.17	7.40	11.52

Table 2 – Ultimate and proximate analysis of MSW samples.^a

Ultimate analysis		Proximate analysis	
C	51.81 (wt %)	Volatile matter	82.28 (wt %)
H	5.76 (wt %)	Fixed carbon	11.79 (wt %)
O ^b	35.88 (wt %)	Ash	5.93 (wt %)
N	0.26 (wt %)	Low heating value	21 306 kJ/kg
S	0.36 (wt %)	Apparent density	280.5 kg/m ³

^a Dry basis.

^b By difference.

thickness was placed on the catalyst for collecting the char from MSW gasification and uniform distribution of gas through the catalyst bed. During the experiments, the saturated steam of 109.6 °C and 141.3 kPa is produced in a steam generator.

The procedure for a typical steam catalytic gasification experiment is described below. Prior to each experiment, calcined dolomite was held in the stainless tube. The shredded MSW sample was loaded in a hopper. When the desired temperature was reached, MSW feedstock and steam were continuously fed into the gasifier simultaneously with the desired rates, respectively. 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, thereby the fine particles were removed. The condensable matter was quenched as the gas passed through the water condenser. Subsequently, the product gas was dried after entering into a gas meter and a gas dryer. At last heating of the furnace stopped, the steam generator was turned off, and the reactor was cooled to the ambient temperature.

After every 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. The gas produced was combusted after sampling and analysis. In general, it took 20 min for the experiment to reach a stable state, to ensure the reliability of test data, each experiment was repeated two times, and the results were in good agreement. The data reported in this paper are average values of two times.

2.4. Method of sampling and analysis

The low heating value (LHV) of the MSW samples was estimated using a bomb calorimeter (6300, Parr Inc.) with accuracy of <0.15%.

Ultimate analysis of the MSW samples was obtained with a CHNS/O analyzer (Vario Micro cube, Elementar). Such

analysis gives the weight percent of carbon, hydrogen, oxygen, nitrogen, and sulphur in the samples simultaneously, and the weight percent of oxygen is determined by the difference. A TA Instruments system (TGA 2000, Las Navas) was used to obtain proximate analysis of the MSW samples (that is, moisture, volatile matter, fixed carbon, and ash content of the material).

X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V.) measurements of catalysts were carried out to determine main components and investigate the catalytic performance before and after the experiment. Furthermore, the surface characteristics of natural and calcined dolomite were determined using an accelerated surface area porosimetry (ASAP 2010, Micrometrics) instrument, which used liquid nitrogen at 77 K, was applied to measure the BET surface area of natural and calcined dolomite.

The product gas volume was measured using a gas meter (J1.6-II, Wuhan Apollo), and sampled discontinuously using gas bags at regular time intervals. Gas composition analysis was conducted with a dual channel micro-gas chromatography (Micro-GC 3000A, Agilent) that was able to provide precise analysis of the principal gas components (H₂, CO, CO₂, CH₄, C₂H₄ and C₂H₆). The instrument was equipped with TCD and FID detectors, and the carrier gas was helium in all analyses.

2.5. Methods of data processing

Lower heating value (LHV) of hydrogen-rich gas is calculated by,

$$\text{LHV}(\text{MJ/N m}^3) = (\text{CO} \times 126.36 + \text{H}_2 \times 107.98 + \text{CH}_4 \times 358.18 + \text{C}_2\text{H}_2 \times 56.002 + \text{C}_2\text{H}_4 \times 59.036 + \text{C}_2\text{H}_6 \times 63.772)/1000$$

Where, CO, H₂, CH₄, C₂H₄ and C₂H₆ are the molar percentages of components of hydrogen-rich gas, respectively.

Carbon conversion efficiency (%) is calculated by,

$$X_C(\%) = \frac{12Y(\text{CO}\% + \text{CO}_2\% + \text{CH}_4\% + 2 \times \text{C}_2\text{H}_4\% + 2 \times \text{C}_2\text{H}_6\%)}{22.4 \times C\%} \times 100\%$$

Where, Y is the dry gas yield (Nm³/kg), C% is the mass percentage of carbon in ultimate analysis of MSW feedstock, and the other symbols are the molar percentage of components of hydrogen-rich gas.

Steam decomposition (%) is calculated by,

$$\text{SD} = \frac{1000Y(\text{H}_2\% + \text{CH}_4\% + 2 \times \text{C}_2\text{H}_4\% + 3 \times \text{C}_2\text{H}_6\%) \times 18/22.4}{W_1 + W_2} \times 100\%$$

Where, W₁ is steam flow rate and W₂ represents the total moisture content in the MSW feedstock.

Cold gas efficiency (%) is calculated by,

$$= \frac{\text{LHV of product gas (kJ/N m}^3) \times \text{dry gas yield (N m}^3/\text{kg)}}{\text{LHV of feed MSW(kJ/kg)}} \times 100\%$$

Weight hourly space velocity (WHSV) is defined as mass flow rate of MSW fed to the reactor, divided by the mass of catalyst in the catalytic reactor.

Table 3 – Surface characteristics of catalyst.

Catalyst	BET surface area (m ² /g)	Micropore area (m ² /g)	External surface area (m ² /g)	Total pore volume (cm ³ /g)
Calcined dolomite	9.96	1.73	8.23	2.27

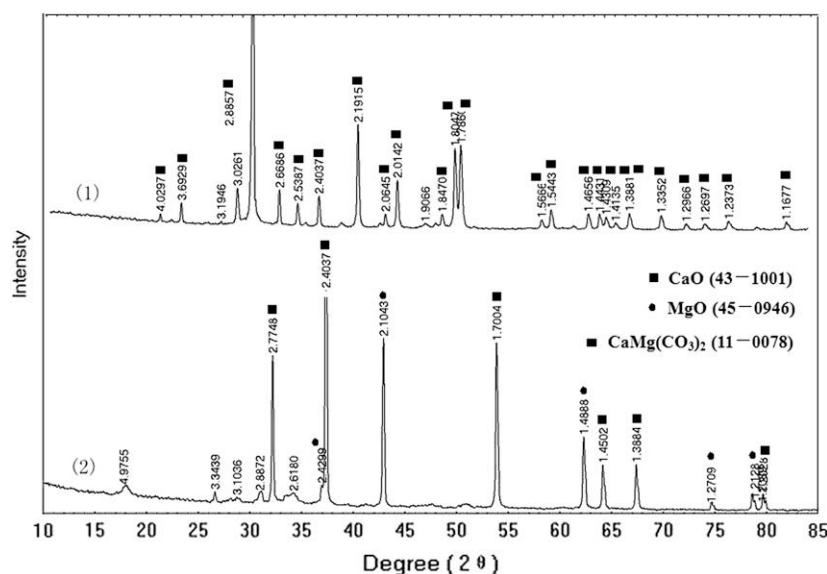
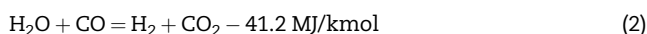
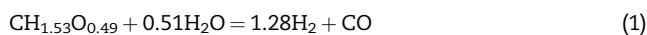


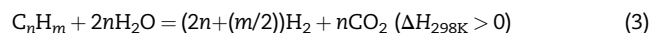
Fig. 1 – XRD patterns of catalysts. (1) natural dolomite, (2) calcined dolomite.

The molecular formula of MSW (daf.) can be expressed as $\text{CH}_{1.53}\text{O}_{0.49}$ based on the ultimate analysis (Table 2). The stoichiometric yield of H_2 from MSW is 106.58 mol H_2 /kg MSW (daf.) calculated by the follow equations:



H_2 potential yield is defined as the sum of measured hydrogen in product gas and the theoretical hydrogen that could be formed by completely shifting carbon monoxide as in

reaction (2) and completely reforming hydrocarbon species in product gas according to reaction (3), given below [30]:



Modeling results were compared with all sets of experimental results and kinetic model data. The sum squared deviation method was used to estimate the accuracy of modeling results [29].

$$\text{RSS} = \sum_{i=1}^N \left(\frac{y_{ie} - y_{ip}}{y_{ie}} \right)^2$$

$$\text{MRSS} = \frac{\text{RSS}}{N}$$

$$\text{Mean error} = \sqrt{\text{MRSS}}$$

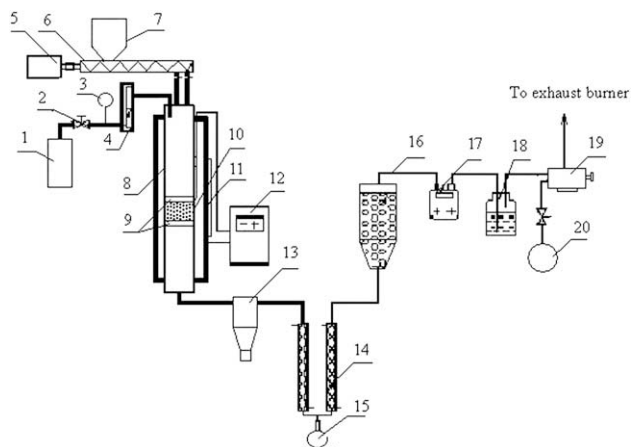


Fig. 2 – Flowchart of experimental apparatus 1, steam generator; 2, valve; 3, piezometer; 4, steam flow meter; 5, motor; 6, screw feeder; 7, hopper; 8, fixed bed gasifier; 9, porous ceramic; 10, catalyst; 11, electric furnaces; 12, temperature controller; 13, cyclone; 14, condenser; 15, flask; 16, filter; 17, gas meter; 18, silica gel; 19, air pump; 20, gas sample bag.

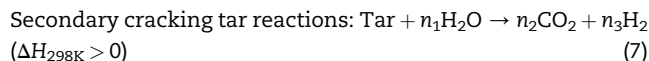
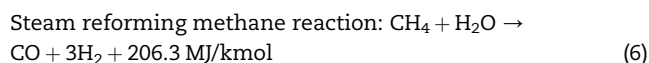
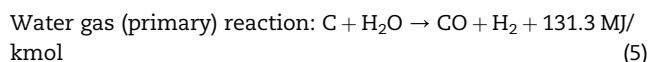
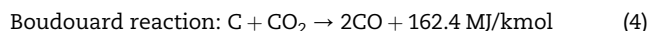
3. Results and discussion

3.1. Mechanism of catalytic steam gasification of MSW

The purpose of using catalyst includes: (1) cracking of tar; (2) to increase MSW conversion; (3) to enhance steam reforming and water gas shift reactions in order to produce hydrogen-rich gas and more product gas.

In general, steam gasification reactions include two steps. The first step is a thermochemical decomposition of MSW with production of tar, char and volatiles, this step termed primary pyrolysis, could perform at a lower temperature of $\sim 300^\circ\text{C}$, and last until a temperature of 700°C or even higher. The second step includes reactions of CO , CO_2 , H_2 and H_2O with the hydrocarbon gases and carbon in MSW, thereby producing gaseous product. The catalytic steam gasification

mechanism of MSW might be described by the following reactions as follows:



Calcined dolomite can accelerate the reaction rate of the steam with tar and char, also participate in the secondary reactions [25]. Furthermore, as shown in Fig. 1, calcined dolomite consists of CaO, and MgO, which convert to Ca(OH)₂ and Mg(OH)₂ quickly in the presence of moisture, some Ca(OH)₂ and Mg(OH)₂ can convert to CaCO₃ and MgCO₃ using CO₂ as a sorbent by reacting with CO₂ produced during gasification reaction [26–28], provided the reaction temperature is appropriately low, such as not much over 700 °C. Thus, calcined dolomite could also be a substantially good CO₂ acceptor for catalytic steam gasification of MSW [29] at lower temperature. Thus, CO₂ absorbing contributes to water gas shift reaction (Eq. (2)), steam reforming hydrocarbon reaction (Eq. (3)) and secondary cracking tar reactions (Eq. (7)), which lead to production of hydrogen-rich gas and high content of combustible gas. At temperatures >800 °C, calcined dolomite exhibits basically the catalytic effect only, which leads the H₂ content of the product gas to increase and the tar release with the gas to decrease [29].

3.2. Influence of steam to MSW ratios

In regard to the gas fraction from catalytic steam gasification of MSW, gas components distribution, LHV, dry gas yield, steam decomposition, carbon conversion efficiency and cold gas efficiency at 900 °C are listed in Table 4 with increasing S/M from 0.39 to 1.04. It indicated that the main components are H₂, CO, CO₂, and a small fraction of low molecular hydrocarbon species (CH₄, C₂H₄ and C₂H₆). The general trend showed an increase of H₂ and CO₂ contents, H₂ yield, H₂ yield potential, dry gas yield, steam decomposition, carbon conversion efficiency as well as cold gas efficiency, and a decrease of CO content, CH₄, C₂H₄ and C₂H₆ contents were relatively small, and slightly changed.

As shown in Table 4, as expected, in the steam gasification process the presence of calcined dolomite caused a slight increase in dry gas yield from 0.45 N m³/kg, in the non catalytic process, up to 0.68 N m³/kg. There was also a significant increase in the H₂ content (from 27.50% to 32.62%), H₂ yield (from 6.06 to 10.86 mol/kg), and CO content (from 20.80% to 55.57%). While, CO₂ content (from 22.90% to 10.91%), CH₄ content (from 0.041 down to 0.007), C₂H₄ content (from 7.74% to 0.2%), and C₂H₆ content decreased (from 8.34% down to 0.1%), with the use of the catalyst. It was concluded that calcined dolomite revealed better catalytic performance at the presence of steam.

The product distribution (gas, tar and char) profile listed in Table 4 indicated that mass balance exceeds 100% due to the introduction of steam. With S/M increasing from 0.39 to 1.04, the gas increased gradually from 87.60% to 98.71%, while the char decreased significantly from 16.69% to 9.91%, Especially, the tar catalytic gasification was improved drastically, tar decreased drastically from 0.32% to 0.11% as S/M increased from 0.39 to 0.60, in particular, no condensed matter was observed in the cleaning system as S/M increased from 0.68 to 1.04. This was quite expected since increasing the amount of steam, being one of the reactants, in the reaction led to higher conversion as well as higher gas production.

In regard to the gas fraction, H₂ content increased from 32.62% to 53.22%, it was concluded that higher S/M significantly resulted in higher H₂ content. It was because that more steam favored water gas shift reaction (Eq. (2)), steam reforming methane reaction (Eq. (6)), steam reforming heavier hydrocarbon reaction (Eq. (3)) and carbon gasification reaction (Eq. (5)), together with the secondary cracking tar reactions (Eq. (7)), which were the main factors responsible for the increase in H₂ content, which agreed with the results of Wei et al. [25]. CH₄, C₂H₄ and C₂H₆ contents were relatively small, and slightly changed. This indicated that S/M almost had no influence on the decomposition of CH₄, C₂H₄ and C₂H₆. Meanwhile, dry gas yield increased from 0.68 to 1.65 N m³/kg of MSW, carbon conversion efficiency and cold gas efficiency increased from 47.59% to 80.19% and from 34.39% to 70.40%, respectively, those are quite expected due to more steam introduced during the gasification process, therefore, more steam can improve the quality of product gas. Furthermore, the lower heating value (LHV) of hydrogen-rich gas slightly decreased from 10.78 to 9.09 MJ/N m³, thus the product gas also can be directly used as a fuel with medium heating value (~15 MJ/N m³). However, the energy content of the total hydrogen-rich gas almost doubled from 28.08 to 59.83 MJ/N m³.

Furthermore, CO₂ content increased from 10.91% to 20.61%, while CO content decreased from 55.57% to 25.72%, thus, the CO/CO₂ molar ratio decreased as listed in Table 4, moreover, the H₂/CO molar ratio increased, which was in agreement with results of Gao et al [30]. It was concluded that water gas shift reaction (Eq. (2)) favored H₂ production, and had a more prevalent role during the catalytic steam gasification reactions. Meanwhile, the presence of calcined dolomite accelerated further reactions of heavier hydrocarbons and tars with steam. With respect to the different gas composition, it is well-known that syngas that has different levels of H₂/CO ratios are suitable for different applications: for example, syngas with a H₂/CO ratio in the higher range is advisable for producing hydrogen for ammonia synthesis or for fuel cell applications, whereas syngas with a H₂/CO molar ratio in the range of 1–2 is highly desirable as feedstock for Fischer–Tropsch synthesis for the production of transportation fuels [15], and useful for the chemical industry to synthesise products such as methanol and virgin naphtha [31].

The experimental results showed that such a syngas composition with a H₂/CO molar ratio in the range of 1–2 could be obtained by conducting the experiment over S/M range of 0.5–1.0 at 900 °C. Therefore, by controlling the introduction of steam, H₂/CO molar ratio in the syngas during catalytic steam gasification of MSW can be adjusted to the desired value.

Table 4 – Influence of S/M on product distribution and gas characterization.

Run	1	2	3	4	5	6	7
Steam flow rate, kg/h	0.117	0.117	0.138	0.180	0.204	0.231	0.312
MSW feeding rate, kg/h	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Steam to MSW ratio (S/M)	0.39	0.39	0.46	0.60	0.68	0.77	1.04
WHSV, h ⁻¹	– ^a	1.51	1.47	1.40	1.32	1.29	1.22
Catalyst, kg	0	0.200	0.204	0.214	0.227	0.233	0.246
Product distribution (wt %)							
Gas	82.73	87.60	91.32	94.33	96.69	97.93	98.71
Tar	0.49	0.32	0.11	0.07	0	0	0
Char	19.52	16.69	14.31	13.48	11.47	10.62	9.91
Gas composition, mol % (dry basis)							
H ₂	27.50	32.62	42.92	43.30	51.70	51.94	53.22
CO	20.80	55.57	45.33	39.33	28.91	27.57	25.72
CO ₂	22.90	10.91	11.28	16.96	18.65	19.80	20.61
CH ₄	12.72	0.60	0.40	0.31	0.21	0.40	0.23
C ₂ H ₄	7.74	0.20	0.01	0.60	0.21	0.14	0.17
C ₂ H ₆	8.34	0.10	0.06	0.04	0.32	0.15	0.05
H ₂ /CO	1.32	0.59	0.95	1.10	1.79	1.88	2.07
CO/CO ₂	0.91	5.09	4.02	2.32	1.55	1.39	1.25
H ₂ yield (mol/kg)	6.06	10.86	19.11	21.40	30.11	32.54	42.98
H ₂ yield potential (mol/kg)	40.98	28.08	36.70	39.57	45.13	47.43	59.83
LHV (MJ/N m ³)	15.02	10.78	10.51	9.79	9.34	9.25	9.09
LHV (MJ/kg of fed MSW)	6.72	7.33	9.56	9.89	11.12	11.84	15.00
Dry gas yield (N m ³ /kg)	0.45	0.68	0.91	1.01	1.19	1.28	1.65
Steam Decomposition (%)	28.51	15.92	27.10	30.99	43.17	46.41	60.61
Carbon conversion efficiency (wt %)	44.07	47.59	53.77	60.45	60.08	63.99	80.19
Cold gas efficiency (%)	31.72	34.39	44.88	46.42	52.18	55.88	70.40

a Non catalytic steam gasification process.

Meanwhile, Fig. 3 shows that H/C atomic ratios of the hydrogen-rich gas increased sharply from 0.81 to 2.19 as S/M increased from 0.39 to 0.68, whereafter with a slight increase due to more H₂ obtained in the product gas. O/C atomic ratios slightly increased, when S/M increased from 0.39 to 1.04 because of more CO₂ obtained.

Furthermore, Fig. 4 shows gas composition profile of H₂, CO, CO₂, CH₄, C₂H₄ and C₂H₆ with reaction time, with S/M of 0.46 and at a WHSV value of 1.47 h⁻¹. It took 20 min for the experiment to reach a stable state, thereafter, H₂, CO, CO₂, CH₄, C₂H₄ and C₂H₆ contents remained almost constant throughout the experiment with reaction time, and CH₄, CH₄

and C₂H₆ contents show very low, close to zero. These results indicated that calcined dolomite revealed good catalytic performance, and did not deactivate under these operating conditions.

3.3. Influence of weight hourly space velocity (WHSV)

The influence of WHSV on gas composition at S/M of 0.46 was investigated, the value of WHSV ranged between 1.22 and 1.51 h⁻¹. The gas composition profile from catalytic steam gasification of MSW is plotted in Fig. 5, a decrease of WHSV produced an increase of H₂ and CO₂ contents as well as LHV, dry gas yield, H₂ yield, H₂ yield potential, steam

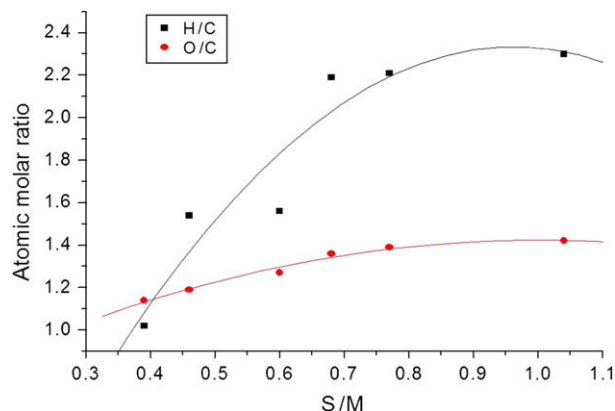


Fig. 3 – H/C and O/C atomic ratios of the product gas at different S/M.

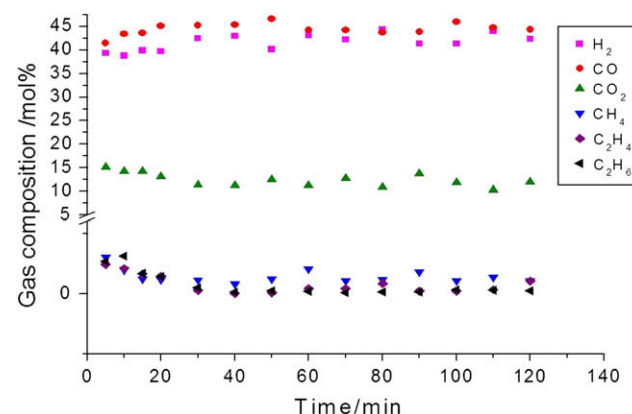


Fig. 4 – Gas composition versus time.

decomposition, and a decrease of CO content. The contents of CH_4 , C_2H_4 and C_2H_6 were relatively small, and the influence of WHSV was insignificant. It was explained by the presence of more calcined dolomite namely lower WHSV value, which revealed better catalytic activity, and improved the quality of the product gas and diminished significantly the tar yield. Table 3 shows that calcined dolomite is porous with high external surface area and micropore area, the large external surface area of calcined dolomite particles accounts for the high chance of gas contacting solid particles and long gas residence time of >4 s. On the other hand, WHSV indicates the gas residence time in the catalytic gasification reactor [32], lower WHSV value means longer gas residence time, which can promote tar adsorbing and improve the catalytic cracking of hydrocarbon and the elimination of tar.

3.4. Comparison between gas composition and thermodynamic equilibrium calculations

To verify whether the experimental gas reached thermodynamic equilibrium, the chemical equilibrium calculations were performed using a well-known equilibrium model: GasEq model developed by Chris Morley [33] (GasEq Version 0.79, 2005). It was considered useful to compare the experimental gas composition with that corresponding to thermodynamic equilibrium, because a kinetic model can be developed by using the experimental gas composition data in a state of equilibrium. Fig. 6 shows this comparison for S/M of 0.39, 0.46, 0.60, 0.68, 0.77 and 1.04, a good agreement was achieved between the experimental gas composition and thermodynamic equilibrium results calculated from GasEq model. Furthermore, the error analysis of data for gas composition listed in Table 5 indicated that H_2 had the lowest error, while C_2H_4 and C_2H_6 had the highest error due to extremely low contents in product gas, and contents corresponding to thermodynamic equilibrium were zero. It was concluded that the presence of calcined dolomite was efficient to modify gas composition in a state of thermodynamic equilibrium. The results obtained are useful for the development and optimization of MSW gasification kinetic model.

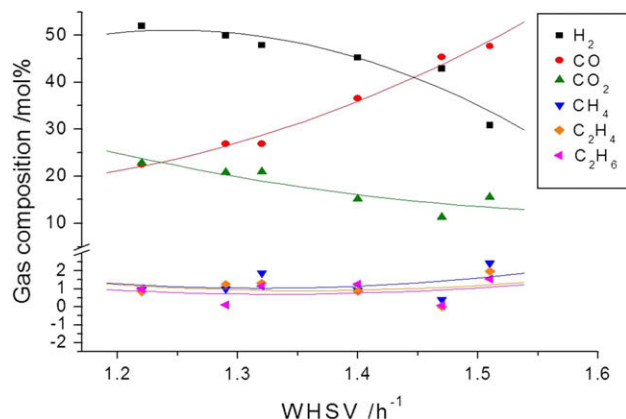


Fig. 5 – Influence of WHSV on gas composition at S/M of 0.46.

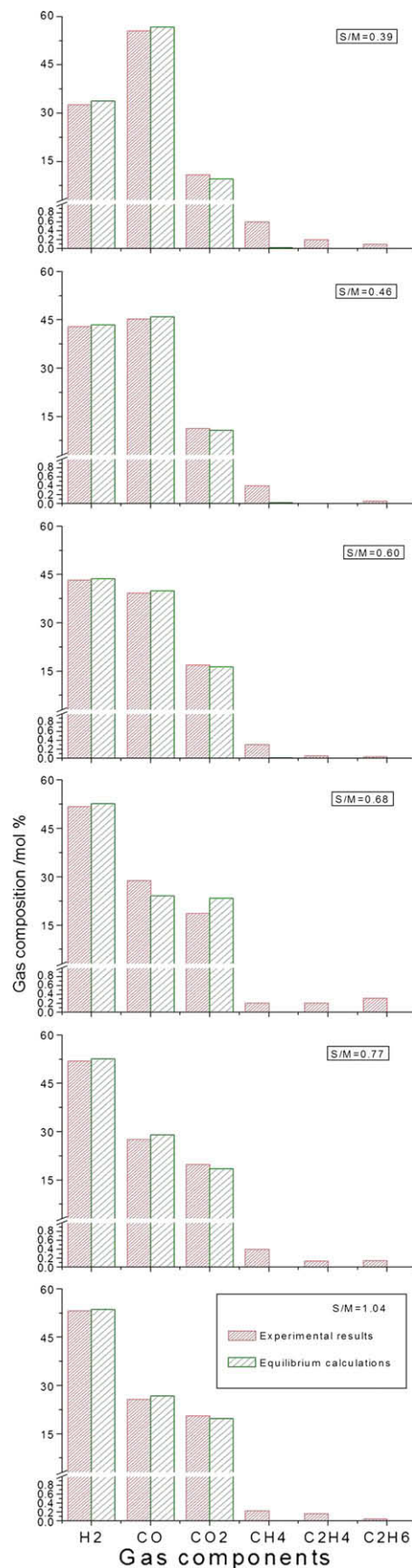


Fig. 6 – Comparison between experimental results and thermodynamic equilibrium calculations for different S/M.

Table 5 – Error analysis of data.

Data	Gas composition (dry basis)						H ₂ yield	C-conv. efficiency
	H ₂	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	Y _H	X _C
Mean error	0.0175	0.0740	0.1236	0.9809	1.0000	1.0000	0.2628	0.0582

3.5. The kinetic model of catalytic steam gasification of MSW

X_{H_2} , X_{CO} , X_{CH_4} , $X_{C_2H_4}$, $X_{C_2H_6}$

In general, steam gasification reactions include reactions of CO₂, H₂ and H₂O with the combustible fraction of carbon in biomass or coal, thereby producing gaseous product, the essential features involve chemisorption of the reacting gas species on the carbon surface. Similarly, in the steam-carbon reaction during MSW gasification, the chemisorption step involves dissociation of water at the carbon surface into hydrogen atom and a hydroxyl radical, which adsorbs on adjacent carbon sites [20]. Therefore, carbon conversion, hydrogen yield and steam to MSW ratio are very important experimental variables. GasEq model has verified that the experimental gas was in a state of thermodynamic equilibrium, thus kinetic analysis was proposed by using the experimental gas composition data valuable for the in-depth exploration and confirmation of gasification process mechanism. According to the developed mechanism of catalytic steam gasification of MSW, associated with results and discussion concerning the influences of S/M and WHSV on gas production and composition, a corresponding kinetic model was proposed as follows.

Carbon conversion efficiency (X_C) and H₂ yield (Y_H) during MSW steam gasification was modeled with respect to S/M as follows:[34]

$$\frac{dX}{d_{S/M}} = K(1 - X) \quad (8)$$

$$\frac{dX_C}{d_{S/M}} = K_C(1 - X_C) \quad (9)$$

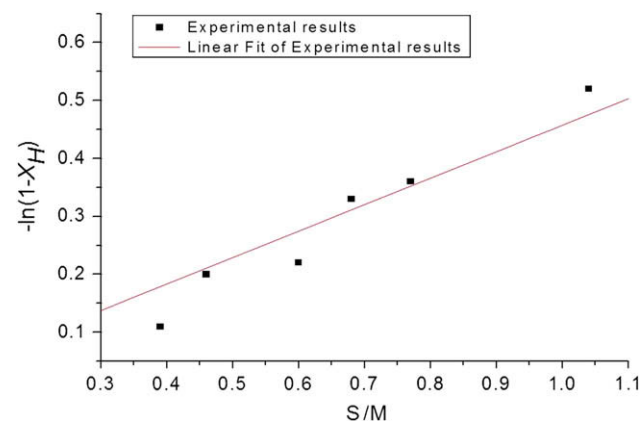


Fig. 7 – Plot of $[-\ln(1 - X_H)]$ vs S/M, a comparison between experimental results and the kinetic model.

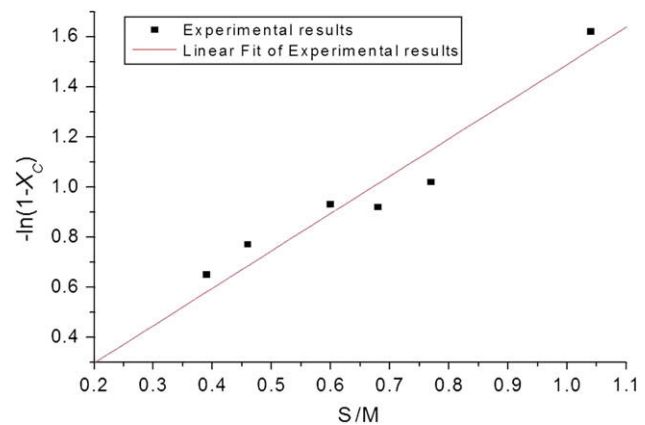


Fig. 8 – Plot of $[-\ln(1 - X_C)]$ vs S/M, a comparison between experimental results and the kinetic model.

$$\frac{d(Y_H/SY_H)}{d_{S/M}} = K_H(1 - Y_H/SY_H) \Rightarrow \frac{dX_H}{d_{S/M}} = K_H(1 - X_H) \quad (10)$$

Where, $X_H = Y_H/SY_H$, SY_H is the stoichiometric yield of H₂ from MSW of 106.58 mol H₂/kg MSW (daf.). The kinetic parameters k_C and k_H can be considered as measures of ability in carbon conversion and hydrogen yield for catalytic steam gasification of MSW. Through integration and rearrangement, the following exponential-type equation can be deduced:

$$X_H = 1 - \exp(-k_H S/M) \quad (11)$$

$$X_C = 1 - \exp(-k_C S/M) \quad (12)$$

$$-\ln(1 - X_H) = k_H S/M \quad (13)$$

$$-\ln(1 - X_C) = k_C S/M \quad (14)$$

As shown in Figs. 7 and 8, it was clear that the kinetic model can describe well the variation of H₂ yield and carbon conversion efficiency with S/M. When the correlation factor R of the model for H₂ yield and carbon conversion efficiency at different S/M are 0.95 and 0.96, respectively, and the kinetic parameter k_H and k_C value are 0.458 and 1.49, respectively, this kinetic model gives a good agreement with the experimental gas composition data of catalytic steam gasification of MSW, which was further justified by the error analysis of data for carbon conversion efficiency and H₂ yield shown in Table 5. Carbon conversion efficiency and H₂ yield had rather low error in all sets of experiments.

4. Conclusions and future work

Steam gasification offers an attractive alternative option for the treatment and energy utilization of MSW. The steam gasification of MSW using calcined dolomite as a catalyst into

hydrogen-rich gas or syngas, was performed in a fixed bed reactor at 900 °C over the S/M range of 0.39–1.04, for weight hourly space velocity (WHSV) in the range of 1.22–1.51 h⁻¹. In a series of trials, the influence of S/M on gas production and composition was investigated. The data showed that calcined dolomite revealed good catalytic performance for steam gasification of MSW, more steam introduced can enhance the H₂ yield and H₂ yield potential, and improve MSW gasification. H₂ content of 53.22 mol %, H₂ yield of 42.98 mol H₂/kg MSW and H₂ potential yield of 59.83 mol H₂/kg dry MSW, which is 56.14% of the stoichiometric yield (106.58 mol H₂/kg MSW (daf.)), were obtained at the highest S/M level of 1.04.

The steam to MSW ratio played a great role on gas product and composition. Higher S/M resulted in higher conversion of MSW into hydrogen-rich gas or syngas with a significant increase of H₂ content from 32.63% to 53.22%, with S/M increasing from 0.39 to 1.04, H₂ and CO₂ contents increased while CO and CH₄ decreased. Furthermore, the H₂/CO molar ratio, dry gas yield and steam decomposition increased, while CO/CO₂ molar ratio and LHV of syngas decreased. At the presence of steam, calcined dolomite revealed better catalytic performance.

A good agreement was achieved between the experimental gas composition and that corresponding to thermodynamic equilibrium data calculated using GasEq model and further justified by error analysis of data. It was concluded that the experimental gas reached thermodynamic equilibrium. Consequently, a kinetic model was proposed for describing the variation of carbon conversion efficiency and H₂ yield with S/M during the catalytic steam gasification of MSW. The kinetic model revealed a good performance between experimental results and the kinetic model further justified by error analysis of data with a high accuracy over the ranges of experimental conditions examined.

Further work would help to support much better applicability of the present work. Such further work includes: (1) to study catalyst regeneration or pre-treatment; (2) to analyze in detail energy balance of the global catalytic gasification process; (3) experiments with MSW in the presence of oxygen or a mixture of oxygen and steam.

Acknowledgment

The authors wish to acknowledge the financial support received from the National Natural Science Foundation of China (No. 20876066), Hubei Province Scientific and Technological Project Foundation (No. 2007AA204B01) and Hubei Province Transformation Foundation of Scientific and Technological Achievements in Agriculture (No. 2008GB2D100208). The authors would also like to thank the Analytical and Test Center of Huazhong University of Science and Technology for carrying out the analysis of MSW samples.

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