

A STUDY ON THE COMBUSTION OF SOLID FUEL OBTAINED BY HYDROTHERMAL TREATMENT OF THE MUNICIPAL SOLID WASTE

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Abstract: In this study, combustion behavior of hydrothermal treated municipal solid waste was experimentally investigated by its thermogravimetric analysis in nitrogen and air environments. The kinetic parameters of the combustion process were calculated using the reaction order model and the diffusion model (D_3) to predict the combustion reaction mechanism of hydrothermal treated municipal solid waste and compare with Indonesian brown coal. Simultaneously, also from the thermogravimetric analysis data, the combustion characteristics index of hydrothermal treated municipal solid waste and Indonesian brown coal were calculated. The experimental results could help to orient the use hydrothermal treated municipal solid waste for industrial combustion processes.

Keywords: Hydrothermal treatment, Municipal solid waste (MSW), Indonesian brown coal (IBC), Combustion characteristic

NOMENCLATURE:

ASTM - American Society for Testing and Materials

HTM - Hydrothermal treated municipal solid waste

IBC - Indonesian brown coal

MSW - Municipal solid waste

MT - Metric ton

TGA - Thermogravimetric analysis

wt% - Weight percent

k - Rate constant

A - Pre-exponential factor, $\text{mg}^{1-n}/\text{min}$

E_a - Activation energy, kJ/mol

R - Ideal gas constant, kJ/(mol*K)

n - Reaction order

α - Mass conversion ratio, %

T - Temperature, K

t - Time, s

D_i - Ignition index

D_b - Burnout index

S - Integration combustion index

β - Heating rate, °C/min

I. INTRODUCTION

Urbanization coupled with population growth has generated an increasing amount of waste in Vietnam. The total amount of municipal solid waste (MSW) was 27 million metric ton (MT) in 2015 and would reach to 54 million MT of waste by 2030 [1]. However, waste management and treatment in Vietnam are labor-intensive and inefficient. According to the statistics of the General

Department of Vietnam Customs, Vietnam imported totally 43.85 million MT of coal (15.4 million MT from Indonesia, 15.7 million MT from Australia and others...) [2]. The domestic coal consumption was 65.5 million tons in 2020 [3] meanwhile a large amount of MSW was not able to use for energy production.

The typical MSW in Vietnam is rich in organic matter and it has high moisture content. The

hydrothermal process is the treatment of MSW with high water content and the conversion of bound water into free water. When the steam temperature in a range of 200 - 230 °C, the plant's cell membranes are broken down, leading to converting water inside the cell, and in turn turning bound water into free water [4,5]. The decrease in the oxygen and hydrogen content of feedstock during the hydrothermal process (hydrothermal carbonization) is responsible for high energy densification and formation of the carbonized material having a similar composition like coal (hydrothermal treated MSW) [6]. Moreover, the calorific value of hydrothermal treated MSW (HTM) ranged (from 18 to 23 MJ/kg, which is comparable to the calorific value of hydrochar produced from lignocellulosic waste, food waste and sewage sludge. Based on the properties of hydrochar obtained in their study, the authors also suggested that HTM can be potentially used for carbon sequestration, agriculture applications and energy generation [7]. In this study, we will study the kinetics of the combustion stages and combustion characteristics index of HTM compared with Indonesian brown coal (IBC) by means of thermogravimetric analysis in nitrogen and air environments.

II. MATERIAL AND METHODS

2.1. Hydrothermal process

MSW was collected and manually sorted into 9 categories including organic waste, clothes, wood, plastic packaging, rubber, paperboard, hard plastic, garden waste, and inorganic. MSW after pre-treatment is loaded into the hydrothermal system with its main specification was described in Figure 2.1.

Before carrying out the experiment, the hydrothermal reactor (3) was heated to hydrothermal temperature (220 °C) by saturated steam from electricity boiler (4). Then, MSW is fed from the input gate (2) and is mixed continuously in the hydrothermal reactor by the agitator motor (1). The optimal temperature condition for hydrothermal treatment was 220°C and retention time was in a range of 30 - 45 min. Finally, solid product (HTM) was collected at output gate (5) for further analysis. The experiments were carried out three times and averaging data was chosen for discussion.



Figure 2.1. Equipment for hydrothermal treatment of municipal solid waste. (1) Agitator motor, (2) Input gate, (3) Hydrothermal reactor, (4) Electricity boiler, (5) Output gate

2.2. Coal combustion performance research

Proximate analysis of solid fuel was conducted according to ASTM methods such as ASTM D 3173 for moisture content, ASTM D 3174 for ash content, ASTM D 3175 for volatile content, and ASTM D 5865 for calorific value of solid fuel.

Thermogravimetric analysis (TGA) was carried out with the help of a Macro-TGA device system available at Hanoi University of Science and Technology (HUST) with the heating rate of 10 °C/min and the flow rate of nitrogen or oxygen carrier being 50 mL/min.

Thermal characteristics of solid fuel were determined by the results of TGA in nitrogen. The combustion characteristics of solid fuel were calculated by data TG and DTG curves in oxygen environment.

Reaction rate equation normally used in kinetic study has a form as below:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2.1)$$

Where $f(\alpha) = (1 - \alpha)^n$ is relationship formula of degradation and rate constant. The rate constant is expressed as the reaction order (n); the degradation is expressed as the mass conversion

ratio (α) and is determined by equation (2.2). Our study uses the general equation $off(\alpha)$ to determine the optimal reaction order for the reaction process and compare it with the available reaction models.

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (2.2)$$

With m_o , m_t and m_f are initial weight of the sample, its weight in t and final weight. k is the rate constant that can be determined by the Arrhenius correlation:

$$k = A e^{\frac{-E_a}{RT}} \quad (2.3)$$

Where, A is the pre-exponential factor (mg^{1-n}/min), E_a is the activation energy (kJ/mol), and R is the ideal gas constant ($8.314 \cdot 10^{-3}$ kJ/(mol*K)), and T is the reaction temperature.

From Eq. (2.1) and Eq. (2.3):

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n e^{\frac{-E_a}{RT}} \quad (2.4)$$

For a fixed heating rate of β ,

$$dT = \beta dt \quad (2.5)$$

On the other hand, as $\frac{d\alpha}{dT} = \frac{d\alpha}{dt} \cdot \frac{dt}{dT}$, from Eq. (2.1), Eq. (2.3) and Eq. (2.4):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} (1 - \alpha)^n e^{\frac{-E_a}{RT}} \quad (2.6)$$

By following Coats and Redfern methods [8], the integral form of Eq. (2.6) is

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{A}{\beta} \int_0^T e^{\frac{-E_a}{RT}} dT \quad (2.7)$$

Or

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] e^{\frac{-E_a}{RT}} \quad (2.8)$$

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (2.9)$$

With

$$g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n} \quad (2.10)$$

A plot of $\ln \left[\frac{g(\alpha)}{T^2} \right]$ versus $\frac{1}{T}$ is a straight regression line with a slope of $\frac{E_a}{R}$. Therefore, A and E_a can be determined.

With the reaction order model, each value of reaction order (n) for the value $g(\alpha)$ corresponding to the coefficient of regression R^2 high, n is viewed as steps of the reaction and the mechanism of the process.

In this study, the reaction order model (n) and diffusion model (D_3) were used to obtain the kinetics parameters. $g(\alpha)$ a given by 3D-diffusion model [9]:

$$g(\alpha) = [1 - (1 - \alpha)^{1/3}]^2 \quad (2.11)$$

Research based on data TG and DTG curves to calculate the combustion characteristics of solid fuel [10,11]. The ignition index, D_i , and the burnout index, D_b , are determined using Eqs. (2.12 and 2.13), respectively.

$$D_i = \frac{DTG_{max}}{T_{max} \cdot T_i} \quad (2.12)$$

$$D_b = \frac{DTG_{max}}{T_{\Delta 0.5} \cdot T_{max} \cdot T_i} \quad (2.13)$$

Where, T_i is the ignition temperature, DTG_{max} is the peak of the DTG curve, is the maximum value of the mass-loss rate during the combustion process. T_{max} is the corresponding temperature of the DTG_{max} . $T_{\Delta 0.5}$ is the half peak width of the DTG curves, namely the temperature difference between the two temperatures at the mass loss rate of DTG_{max} by a factor of 0.5. Further, one integration combustion index parameter, S , is defined as

$$S = \frac{DTG_{max} \cdot DTG_{mean}}{T_i^2 \cdot T_b} \quad (2.14)$$

$$\text{with } DTG_{mean} = \frac{\alpha_{T_b} \cdot \alpha_{T_i}}{(T_b - T_i) / \beta} \quad (2.15)$$

DTG_{mean} is the average conversion rate from T_i to T_b , and β is the heating rate. T_b is the burnout temperature and can be defined as the temperature at which conversion (α) of 98% is achieved during one combustion stage or the entire process. S is the integration parameter of ignition and burnout characteristic for combustion, and the higher the S value is, the better the combustion characteristics are.

III. RESULTS AND DISCUSSIONS

3.1. Technical composition of solid fuel

Table 3.1 summarises proximate analysis of hydrothermal treated municipal solid waste (HTM)

Table 3.1. Proximate analysis of hydrothermal treated municipal solid waste (HTM) and Indonesian brown coal (IBC)

Proximate analysis (wt%)	HTM	IBC
Moisture (ad)	18.0	15.8
Ash (db)	19.97	10.30
Volatile (db)	56.3	48.2
Fixed carbon (db)	23.73	41.5
Higher heating value (db-Kcal/kg)	4.491	5.603

Note: ad: Air dry basis; ab: Dry basis

and Indonesian brown coal (IBC). The results show that the volatile matter content of HTM is higher than that of IBC (56.3 vs 48.2 %wt). The volatile matter content characterizes the flammability of coal, so it can be expected that the flammability of HTM is higher than that of IBC. However, the water and ash content of HTM is much higher than that of IBC. In contrast, fixed carbon content of HTM is lower than of IBC (23.73 vs 41.5 %wt). Therefore, the calorific value of HTM is lower than that of IBC (4.491 vs 5.603 Kcal/kg).

3.2. Thermal characteristics of solid fuel

Figure 3.1 shows the TGA curves of HTM and IBC in nitrogen and air environments. The results show that the temperature below 150 °C is a dehydration of moisture (physical moisture and chemical moisture) in solid fuels, so the weight loss of the samples is similar in both environments. The weight loss is about 15 %wt during this period. The

mass reduction of solid fuel samples started differently in nitrogen and air when the temperature is higher than 150 °C. During this period, the difference between the weight loss in nitrogen and air of the IBC is higher than that of the HTM. Specifically, IBC is lost about 55 %wt in nitrogen environment and 89 %wt in air atmosphere at 800 °C. This value is about 64 %wt and 85 %wt for HTM, respectively. This can be explained by the difference in fixed carbon content of HTM and IBC. The fixed carbon content in IBC is higher than that in HTM (38.1% vs 21.81%), so IBC is less degraded than HTM in nitrogen environment. On the other hand, through the comparison of thermal analysis results of HTM and IBC, it can be seen that the process of releasing volatiles and burning of IBC only occurs in one stage while HTM occurs in two stages. The weight loss of IBC is about 73.84 %wt in air atmosphere

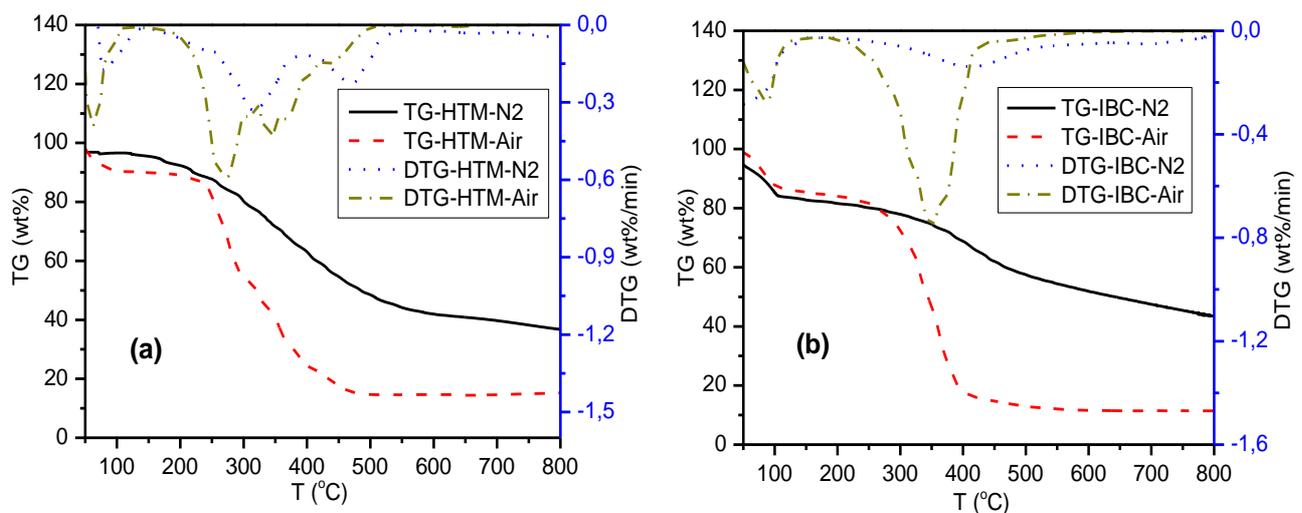


Figure 3.1. TGA curves of HTM (a) and IBC (b) in nitrogen and air environment at a heating rate of 10°C/min

and it occurs continuously over the temperature range of 150 - 550 °C. This means that the process of releasing volatiles and burning of fixed carbon in IBC occur simultaneously on the surface of the solid fuel until it is extinguished. Meanwhile, the weight loss of HTM is about 40.05 %wt in 150 - 320°C and 35.61 %wt in 320 - 520°C. At the temperature period of 150 - 320°C, HTM occurs decomposition and evaporation of the corresponding compounds in MSW after hydrothermal process such as lignocellulose compounds in biomass, polymer compounds with mass low molecular weight in plastic, nylon, fabric or other organic compounds. The process of releasing volatiles and burning of fixed carbon occurs during the temperature period of 320 - 520°C. Through these analysis results, our research predicts that HSF occurs homogenous

combustion (burning in the vapor phase) in the temperature range of 150 - 320°C and heterogeneous combustion (burning in solid phase) in the temperature range of 320 - 520°C.

3.3. The combustion characteristics of solid fuel

Based on the results of thermal characteristic analysis, our study calculates the kinetic parameters in the combustion process of IBC and HTM. Equations (2.9), (2.10) and (2.11) were used for the calculation and the results are shown in Table 3.2. The mechanism of the combustion reaction can be predicted by comparing the activation energy (E_a) according to the reaction order model and the diffusion model (D_3). The results show that, HTM occurs combustion according to the kinetic model of order 2.5 ($n = 2.5$)

Table 3.2. Kinetic parameters of solid fuels in an oxidative environment at a heating rate of 10°C/min

Samples	Temperature range (°C)	Reaction order model				D_3 -diffusion model		
		n	E_a (kJ/mol)	A (min ⁻¹)	R ²	E_a (kJ/mol)	A (min ⁻¹)	R ²
HTM	150 - 320	2.5	45.2	1.68×10 ⁴	0.99	48.2	1.12×10 ²	0.91
	320 - 520	3.0	53.2	1.70×10 ⁴	0.99	27.3	0.02×10 ²	0.94
IBC	150 - 550	2.0	37.6	3.25×10 ²	0.91	48.1	0.96×10 ²	0.92

Table 3.3. Analytical data from TG/DTG curve of solid fuels samples in the air environment at a heating rate of 10 °C.min⁻¹

Samples	Temperature range (°C)	Weight loss (wt%)	T _i (°C)	T _b (°C)	T _{Δ0.5} (°C)	T _{max} (°C)
HTM	150 - 320	40.05	247	317	80	274
	320 - 520	35.61	334	476	72	343
IBC	150 - 550	73.84	299	498	85	352

Table 3.4. Total combustion characteristics of solid fuel samples

Samples	Temperature range (°C)	Total combustion characteristics index		
		D _i ×10 ⁶ (wt%.min ⁻¹ .°C ⁻²)	D _b ×10 ⁸ (wt%.min ⁻¹ .°C ⁻³)	S×10 ⁸ (wt% ² .min ⁻² .°C ⁻³)
HTM	150 - 320	8.73	10.96	35.53
	320 - 520	3.69	5.11	4.68
IBC	150 - 550	7.24	8.51	6.96

with an activation energy value of 45.2 kJ/mol during the temperature period of 150 - 320°C. At the same time, the activation energy value in this period is 48.2 kJ/mol with the diffusion model. That means that the combustion of HTM obeys the diffusion model in the temperature range of 150 - 320°C. In other words, the combustion of HTM occurs in the homogeneous phase (burning in the vapor phase) in 150 - 320°C. At the temperature stage of 320 - 520°C, the combustion process of HTM obeys the 3rd reaction order model with an activation energy value of 53.2 kJ/mol. Compared with the results of the activation energy value according to the diffusion model ($E_a = 27.3$ kJ/mol), there is a significant difference. That means that the combustion process of HTM does not obey the diffusion model but the reaction order model. In other words, the combustion of HTM is a heterogeneous combustion process (burning in the solid phase) in the temperature period 320 - 520°C. For IBC coal combustion, it is not possible to separate the homogeneous and heterogeneous combustion process under analytical conditions.

The calculation results of kinetic parameters of the combustion of IBC also show that there is a significant difference in activation energy values according to the reaction order model and diffusion model (37.6 and 48.1 kJ/mol). Thus, the kinetic calculation results have proved the predictions from the TGA thermal analysis results.

Table 3.3 presents the analytical data from TG/DTG curve of HTM and IBC in the air atmosphere at a heating rate of 10 °C.min⁻¹. The IBC takes place the process of releasing volatiles and burning with the ignition temperature (T_i) about 299°C and the burnout temperature (T_b) about 498°C. While the ignition and burnout temperatures of HTM are 247°C and 317°C in the range of 150 - 320°C, respectively. These values are 334°C and 476°C in the range of 320 - 520°C, respectively. This result shows that HSF has the ability to ignite at a lower temperature than IBC but is extinguished faster than IBC. The results in this study are of considerable concordance with published studies. For example, the ignition and burnout temperatures for HTM from raw solid waste sludge are 269.5 and 435.5°C, respectively [12]; lignite coal is 336 and 603°C [13]; or steam coal are 348.1 and 493.4°C [14].

From the TGA data, our study calculates the combustion characteristics index of HTM and IBC, the results are shown in Table 3.4. Because of the homogeneous combustion process in the stage of 150 - 320°C, the ignition index (D_i) and the integration combustion index (S) of HTM are higher than that of IBC. The calculated results in this study are of considerable concordance with published research results for other HTM subjects. According to the research results of Pablo J. Arauzo et al. [12], the combustion process of HTM from raw solid waste sludge is $3.53 \cdot 10^{-8} \text{ wt}\%^2 \cdot \text{min}^{-2} \cdot \text{C}^{-3}$ at heating rate of 10°C/min and an air flow rate of 90 mL/min. Therefore, to effectively use HTM for industrial furnaces, it is necessary to mix HTM with other types of fossil coal. The mixing process will increase the calorific value of coal, prolong the burning time (increase D_b) and at the same time increase the total combustion characteristics index of HTM.

IV. CONCLUSION

The combustion of hydrothermal treated MSW occurs in two stages. The first stage is the process of volatile release and homogeneous combustion (burning in the vapor phase) in the temperature range of 150 - 320°C. At this stage, combustion occurs in the diffusion model with an activation energy of 48.2 kJ/mol. The second stage is the heterogeneous combustion of the remaining volatile matter and the fixed carbon (burning in the solid phase) in the temperature range of 320 - 520°C and it obeys the 3rd reaction order model with an activation energy of 53.2 kJ/mol. Meanwhile, the combustion of Indonesian brown coal only occurs in one stage during the temperature range of 150 - 550°C and it is followed the 2nd reaction order model with activation energy 37.6 kJ/mol. On the other hand, HTM has lower combustion characteristics index than Indonesian brown coal. Therefore, to effectively use HTM for industrial combustion processes, it is necessary to improve the combustion characteristics index by mixing with Indonesian brown coal or with other fossil coals.

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NGHIÊN CỨU ĐẶC TÍNH CHÁY CỦA NHIÊN LIỆU RẮN ĐƯỢC SẢN XUẤT BẰNG QUÁ TRÌNH THỦY NHIỆT CHẤT THẢI SINH HOẠT

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Tóm tắt: Trong nghiên cứu này, đặc tính cháy của nhiên liệu rắn được tổng hợp từ quá trình thủy nhiệt rác sinh hoạt được khảo sát thực nghiệm bằng phân tích nhiệt khối lượng trong môi trường khí nitơ và không khí. Các thông số động học của quá trình cháy được tính toán dựa vào mô hình bậc phản ứng và mô hình khuếch tán (D3) để dự đoán cơ chế phản ứng và tiến hành đánh giá so sánh với than nâu Indonesia. Đồng thời, từ dữ liệu phân tích đã tính toán các chỉ số cháy của nhiên liệu rắn và than nâu Indonesia. Các kết quả thực nghiệm có thể định hướng việc ứng dụng nhiên liệu rắn được sản xuất từ rác thải sinh hoạt cho các lò đốt công nghiệp.