

# Pyrolysis and Char Oxidation of Biomass and Coal Blends: Kinetic Study Using Thermogravimetric Analysis

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**Abstract.** Vietnam as an agricultural country has a high potential in biomass, especially agricultural and forestry wastes. This resource offers a promising way to develop co – combustion technology of biomass and coal in Vietnam and thus tackle the environmental issues. A fundamental research was established to study combustion of Vietnamese rice straw and coal. Blends was made by mixing manually 50% wt. of rice straw and 50% wt. of coal. Pyrolysis in inert gas, char oxidation in oxidizing gases (10 % O<sub>2</sub> in N<sub>2</sub>) and combustion process in oxidizing gases (10 % O<sub>2</sub> in N<sub>2</sub>) were implemented. A particular attention was paid to the behaviour of rice straw/coal blends during thermochemical transformation. Concerning pyrolysis process, the char yield of the mixture is equivalent to weighted sum of the char yield of two solid fuels. During the combustion of the blends, we observed a coupling between pyrolysis and char oxidation. The exothermic oxidation reactions could overheat the sample itself and accelerate the pyrolysis and char oxidation kinetics.

## 1. Introduction

In Vietnam an abundant fossil fuel, coal is used mostly as a principal energy resource to produce heat and electricity. In 2015, electricity production coming from coal fire power accounted for 33.5% and was classified in the second position after hydropower at 38% [1]. The latest “National Power Development Plan” indicated that Vietnam will continue developing coal as the main energy source for electricity production. Coal should contribute to 53.2% of the total power generation by 2030. With the increasing number of coal power plants, Vietnam will have to face to many environmental and socio-economic challenges from coal import to pollution and human health issues.

In parallel, biomass is a promising source of energy to be exploited in order to support national energy security and reduce the dependency to fossil fuels. The largest biomass sources for energy production in Vietnam are crop residues and wood. The crop residues can be classified in two categories – agricultural by-products (rice straw, corn leaves and cobs etc.) and agro-industry by-products (rice husk, bagasse, peanut shells, coffee husks, etc.). The wood fuel consists of sawdust, wood chips and bark [2]. Despite of the low heating value of biomass compared to coal, it remains a promising resource because of its large quantity available [3].



In this context, co-combustion of biomass and coal is an opportunity to take advantage of the domestic green resources and to limit the use of fossil fuel in coal power plants. In order to overcome this issues and to develop this technology in Vietnam, a better expertise and understanding of behaviour of biomass/coal blending during combustion is required. In this study, rice straw and anthracite coal were selected because of their large availability in Vietnam.

In general, the combustion of solid fuel can be decomposed into several steps: (1) drying; (2) pyrolysis process, that consists to release volatile gases; (3) oxidation of volatile matters near the particle; (4) char oxidation that converts the solid carbon into CO<sub>2</sub> [4]. In this work, we concentrated separately on the pyrolysis step in inert environment, on the char combustion and on the whole combustion process considering as fuel successively: rice straw, coal and their mixture.

Several research was investigated to study the kinetic of different nature of coal and biomass. Ruiling Du at al. experimented the pyrolysis of Shenfu coal of China. They determined three zones in which the kinetic mechanism changes was accompanied by a radical change in mass loss. The temperature range of each zone is influenced by the heating rate. In the first one, at the lowest temperature range (105 °C – 386 °C at the heating rate of 25 °C/min), the absorbed gas and the water are vaporized. In the second zone (386 °C – 495 °C at the heating rate of 25 °C/min), the volatile matters are released. The coal is transformed into a semi coke. Finally, this semi coked coal are finally coked (495 °C – 900 °C at heating rate of 25 °C/min). The influence of heating rate was observed more remarkable in the second and the third zone than the first one. [5] [6]. Garima Mishra et al. investigated the pyrolysis of rice straw and found that there are three stages like coal: moisture release (until 150 °C), active pyrolysis (150 °C – 350 °C) and passive pyrolysis (350 °C – 700 °C) [7]. In parallel, the oxidation of these solid fuels was also examined by several research groups [3] [8] [9] [10].

The objective of this work is to study the kinetic of rice straw/coal mixture and to understand the coupling effect occurred in the pyrolysis, char oxidation and the overall combustion process.

## 2. Materials and experiments

### 2.1. Materials

In this study, an anthracite coal (Coal) was taken from Ninh Binh coal-fired power plant, situated in the North of Vietnam. This coal is classed under the “low rank coal” category because of its high ash content and its low burning efficiency. The particle size was in the range 45 – 75 µm. The rice straw “Rom nếp” (RS) was taken in the rural area of Hanoi during harvest season. After being dried under the sunlight for a half day, the sample was milled and sieved to obtain a particle size lower than 200 µm. The proximate analysis, as well as the higher heating value of two materials are shown in the Table 1. The coal has significantly different properties compared to the rice straw because of its higher ash content and lower volatile matters. Characterization tests were carried out at least three times to ensure the measurement’s repeatability.

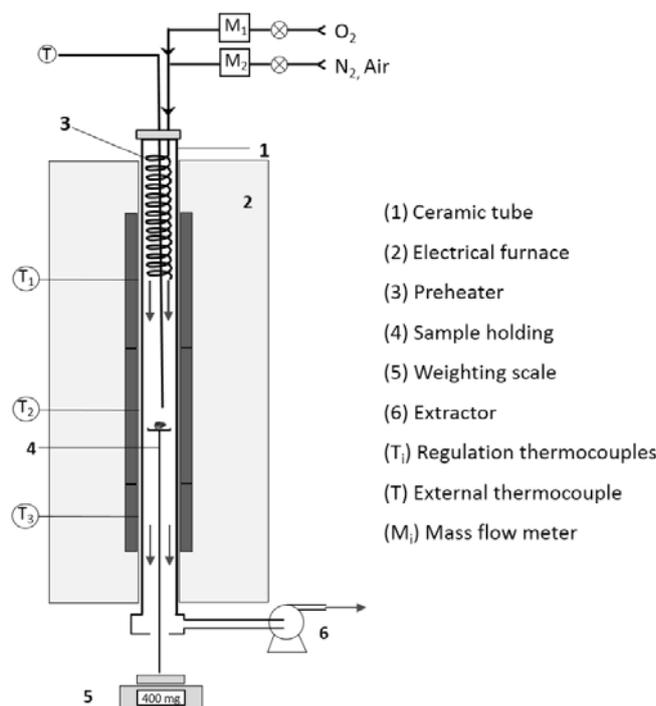
**Table 1.** Proximate analysis of coal and rice straw – dry basis

	FC (%)	A (%)	V (%)	M (%)	HHV (MJ/kg)
<b>Coal</b>	61.39	30.37	8.24	2.51	23.1
<b>Rice straw</b>	15.80	15.48	68.72	9.31	12

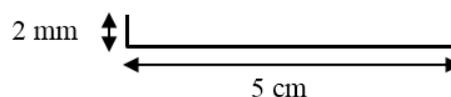
### 2.2. Experiments

The thermo-gravimetric analysis using a macro TG reactor set up at USTH was investigated in non-isothermal operation mode (Figure 1). The temperature and the mass of the sample were recorded continuously. The temperature surrounding the sample is measured in the position of 2 cm above the

crucible. The equipment consisted of a reactor (1), an electrical furnace (2), three thermocouples ( $T_i$ ) and a micro balance (Precisa ES 320A) (5). The maximum heating rate allowed by the system was  $5\text{ }^\circ\text{C}/\text{min}$ . The different gases are mixed before entering the reactor and controlled by the mass flow meter – controllers ( $M_i$ ) with a range of  $0 - 10\text{ NL}/\text{min}$ . The oxygen concentration can be controlled from 0 to 100% by adjusting the mass flow rates of  $\text{N}_2$  and  $\text{O}_2$ . These gases were preheated (3) in a 2-meter-long coiled tube located in the upper part of the reactor.



**Figure 1.** Macro thermo-gravimetric



**Figure 2.** Geometrical view of the alumina crucible

The sample, i.e. rice straw, coal or their blends was weighted to about  $400\text{ mg} \pm 2\text{ mg}$  and was carefully spread on the  $5\text{ cm} \times 2\text{ mm}$  alumina crucible (Figure 2). When operating with the mixture of rice straw and coal, the blends was prepared manually in the proportion of  $50\% \text{ wt.} - 50\% \text{ wt.}$ . The total gases flow rate was set to  $5\text{ NL}/\text{min}$ . For combustion process, the concentration of oxygen in nitrogen was fixed to 10% and assured by adjusting the mass flow rate of  $\text{O}_2$  and  $\text{N}_2$ . Before starting experiments, the gas mixture was circulating inside the reactor for at least 20 minutes to flow out the eventual residual gases. The sample was positioned in the center of the reactor. The reactor was then heated from ambient temperature to the desired temperature with a heating rate of  $5\text{ }^\circ\text{C}/\text{min}$ .

Three series of experiments were performed independently: pyrolysis, char oxidation and combustion. Regarding the pyrolysis, the sample was heated to  $950\text{ }^\circ\text{C}$  in 100%  $\text{N}_2$ . Concerning the char oxidation experiments in the atmosphere of 10%  $\text{O}_2$ , the char of rice straw and coal were produced by pyrolyzing the raw material during 7 minutes at  $900\text{ }^\circ\text{C}$  in a muffle furnace. The char sample was then heated to  $900\text{ }^\circ\text{C}$ . The combustion process experiments were performed in the same experimental condition as char oxidation but using the raw samples.

Some preliminary tests were done to identify the isothermal zone in the reactor and thus the best position for the sample and to check the accuracy of the equipment at high temperature. For the identification of the isothermal zone, a temperature profile was measured along the reactor at different temperature ( $700\text{ }^\circ\text{C}$ ,  $800\text{ }^\circ\text{C}$  and  $900\text{ }^\circ\text{C}$ ). The tests showing that sample could be placed between  $41\text{ cm} - 57\text{ cm}$  from the bottom of the reactor. For all following experiments, the sample was put at the position of  $41\text{ cm}$  from the

bottom. To check the accuracy of the system, some “blank tests” were carried out without sample. A deviation less than 2 mg per hour was found. It was accepted compared to the mass of the sample.

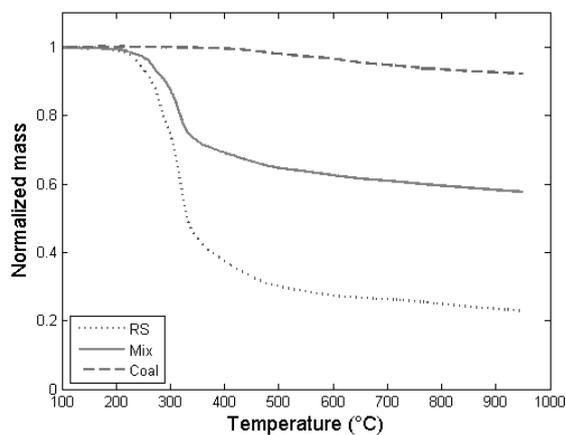
### 3. Results and discussion

For the whole study, the mass loss is presented (Equation 1) by its normalized mass ( $m^*$ ) based on the initial mass of dry sample  $m_{i(dry)}$ .

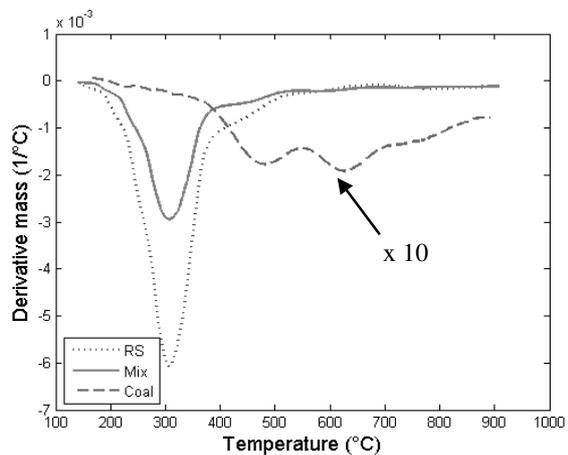
$$m^* = m/m_{i(dry)} \quad (1)$$

#### 3.1. Pyrolysis process of coal, rice straw and their mixture

The Figure 3 and Figure 4 show respectively normalized mass loss (TG curve) and derivative mass loss (DTG curve) of rice straw, coal and their mixture during pyrolysis process under  $N_2$  atmosphere. Because of its low volatile matters, the coal DTG was much lower than the one of rice straw and the mixture. Note that the derivative mass of coal in the Figure 4 has been multiplied by 10 to facilitate the reading.



**Figure 3.** Normalized mass loss versus temperature during pyrolysis process of rice straw, coal and mixture – dry basis.

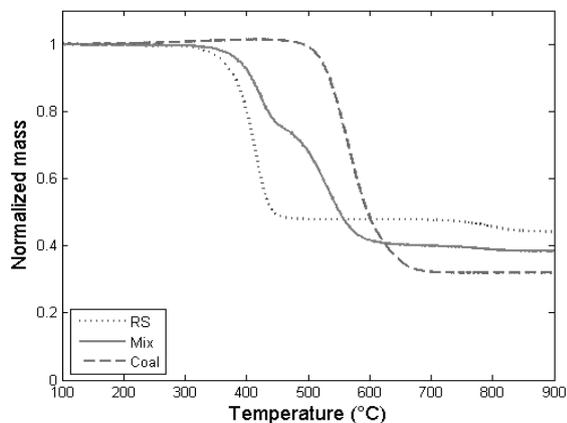


**Figure 4.** Derivative mass loss versus temperature during pyrolysis process of rice straw, coal and mixture.

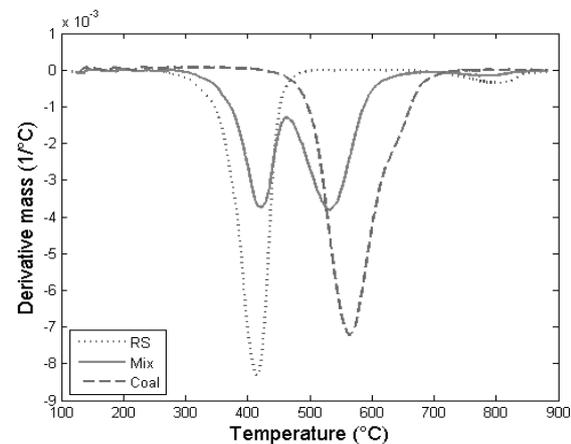
The char yield of rice straw (22.8 %) is significantly lower than coal’s one (92.3 %). The reason is obviously the very high difference in volatile matters content. The char yield of rice straw/coal mixture is 57%. This char yield of the mixture is equivalent to the weighted sum of the char yield of the two constitutive solid fuels. The maximum mass loss is measured at low temperature for rice straw ( $T_{DTG\ max} = 308^\circ C$ ) and for mixture ( $T_{DTG\ max} = 307^\circ C$ ), and at higher temperature for coal ( $T_{DTG\ max} = 480$  and  $627^\circ C$ ). The pyrolysis of rice straw and mixture occurs in a narrow temperature range compared to the pyrolysis of coal. Moreover, the rice straw pyrolysis starts at a lower temperature than the blends pyrolysis. It seems that the presence of coal in the mixture delays the reaction. The temperature  $T_{DTG\ max}$  and the derivative mass loss of each sample are summarized in the Table 2.

#### 3.2. Oxidation process of char of coal, rice straw and their mixture

The Figure 5 and Figure 6 show respectively normalized mass loss (TG curve) and derivative mass loss (DTG curve) of char of rice straw, coal and their mixture during oxidation process under oxidizing atmosphere (10%  $O_2$  in  $N_2$ ).



**Figure 5.** Normalized mass loss versus temperature during oxidation process of char of rice straw, coal and mixture – dry basis.



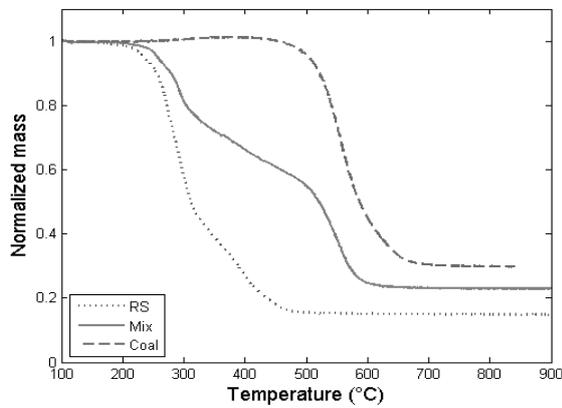
**Figure 6.** Derivative mass loss versus temperature during oxidation process of char of rice straw, coal and mixture.

The oxidation of char from individual feedstock occurs in a narrow range. The mass loss is maximum at the temperature  $T_{DTG\ max} = 416^{\circ}C$  for char of rice straw and  $T_{DTG\ max} = 564^{\circ}C$  for char coal. Their char's mixture oxidation shows two peaks: the first one corresponds to the oxidation of rice straw char and the second one is related to the oxidation of char coal. When mixing char of rice straw and coal, the first char oxidation peak appears at  $T_{max\ DTG} = 421^{\circ}C$ , a slightly higher temperature than for rice straw char alone. The second char oxidation peak is measured at  $T_{max} = 532^{\circ}C$ , a lower temperature than in case of char coal alone. The intensity of the peak is  $-0.0083^{\circ}C^{-1}$  and  $-0.0072^{\circ}C^{-1}$  for rice straw and coal respectively. For the char mixture,  $DTG_{max}$  of the first peak is  $-0.0037^{\circ}C^{-1}$  that represents a half of the char rice straw one.  $DTG_{max}$  of the second peak is  $-0.0038^{\circ}C^{-1}$  that is equivalent to a half of the char coal. The temperature value  $T_{DTG\ max}$  and the derivative mass loss of each sample are summarized in the Table 2

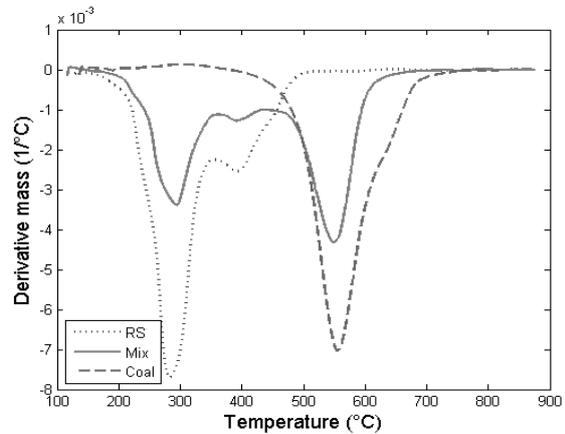
### 3.3. Combustion process of coal, rice straw and their mixture

The Figure 7 and Figure 8 show respectively normalized mass loss (TG curve) and derivative mass loss (DTG curve) of rice straw, coal and their mixture during combustion process under oxidizing atmosphere (10%  $O_2$  and 90%  $N_2$ ).

Figure 8 shows that for rice straw, two zones are identified during combustion. The first zone corresponds to the pyrolysis step and the second one is identified to the oxidation of the produced char [11]. In this case, the maximum mass loss occurs at  $T_{DTG\ max} = 283^{\circ}C$ , tightly lower than temperature in inert atmosphere ( $T_{DTG\ max} = 308^{\circ}C$ ). The same behavior is observed in char oxidation zone, the maximum mass loss during rice straw combustion occurs at lower temperature ( $T_{DTG\ max} = 391^{\circ}C$ ) than in case of char oxidation only ( $T_{DTG\ max} = 416^{\circ}C$ ). Concerning coal combustion, only one peak related to the char oxidation is measured at  $T_{DTG\ max} = 556^{\circ}C$  because of low volatile content. A small gain in mass (normalized mass > 1) is obtained because of some absorption phenomenon at low temperature [12]. Regarding the rice straw/coal mixture, the same observations are the same than those explained for the char oxidation. The first maximum mass loss is measured at  $T_{DTG\ max} = 294^{\circ}C$  and the second maximum mass loss at a temperature  $T_{DTG\ max} = 549^{\circ}C$ . All results are centralized in Table 2. These results show that there is a coupling between pyrolysis and char oxidation when mixing two solid fuels. The oxidation of volatile matters at the end of pyrolysis process overheats the sample and accelerates the oxidation of char.



**Figure 7.** Normalized mass loss versus temperature during combustion process of rice straw, coal and mixture – dry basis.



**Figure 8.** Derivative mass loss versus temperature during combustion process of rice straw, coal and mixture.

**Table 2.** The temperature at maximum mass loss (a) and the maximum DTG (b) of each sample during pyrolysis, oxidation of char and combustion process

	(a) Peak temperature (°C)					
	Coal		RS		Mix	
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
<b>Pyrolysis</b>	480	627	308		307	
<b>Oxidation</b>		564		416	421	532
<b>Combustion</b>		556	283		391	294

	(b) Mass loss rate maximum (1/°C)					
	Coal		RS		Mix	
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
<b>Pyrolysis</b>		$-1,77 \times 10^{-4}$		$-1,92 \times 10^{-4}$	-0,0061	-0,0029
<b>Oxidation</b>		-0,0072		-0,0083	-0,0037	-0,0038
<b>Combustion</b>		-0,007	-0,0077		-0,0025	-0,0034

**4. Conclusion**

The combustion of rice straw, coal and their blends has been experimentally investigated in a new macro TG reactor. Pyrolysis and char oxidation have been studied firstly independently and then the coupled in combustion process was investigated. For pyrolysis experiments, the char yield of the mixture is equivalent to the weighted sum of the two char yield from rice straw and coal. Regarding the combustion process, there is a coupling phenomenon between pyrolysis and char oxidation when mixing two solid fuels. The oxidation reactions near or inside the particles could overheat the sample. Thus, the temperature inside particles may be higher than the temperature measured around the particle. Consequently, this phenomenon could accelerate the char oxidation at lower temperature. Further research could be carried

out to get a better understanding of the interaction and the synergetic effects between coal and rice straw during combustion process. These results could be very useful for further research aiming for industrial application in developing a kinetic model of the combustion.

## 5. References

- [1] EVN 2017 *Vietnam electricity annual report 2016* EVN.
- [2] Arvo Leinonen NDC. Development of biomass fuel chains in Vietnam <http://www.vtt.fi/inf/pdf/technology/2013/T134.pdf> (accessed 12 October 2017).
- [3] Calvo LF, Otero M, Jenkins BM, et al. 2004 Heating process characteristics and kinetics of rice straw in different atmospheres. *Fuel Process Technol* **85** 279–291.
- [4] Boiko EA, Pachkovskii SV. 2004 A kinetic model of thermochemical transformation of solid organic fuels. *Russ J Appl Chem* **77** 1547–1555.
- [5] Du R, Wu K, Zhang L, et al. 2016 Thermal behavior and kinetic study on the pyrolysis of Shenfu coal by sectioning method. *J Therm Anal Calorim* **125** 959–966.
- [6] Wang H, Zhang J, Wang G, et al. 2016 Characteristics and kinetic analysis of co-combustion of brown coal and anthracite. *J Therm Anal Calorim* **126** 447–454.
- [7] Mishra G, Bhaskar T. 2014 Non isothermal model free kinetics for pyrolysis of rice straw. *Bioresour Technol* **169** 614–621.
- [8] Contreras ML, García-Frutos FJ, Bahillo A. 2016 Study of the thermal behaviour of coal/biomass blends during oxy-fuel combustion by thermogravimetric analysis. *J Therm Anal Calorim* **123** 1643–1655.
- [9] Yu Z, Fang S, Lin Y, et al. 2015 Investigation of Rice Straw Combustion by Using Thermogravimetric Analysis. *Energy Procedia* **75** 144–149.
- [10] Wang P, Hedges SW, Casleton K, et al. 2012 Thermal Behavior of Coal and Biomass Blends in Inert and Oxidizing Gaseous Environments. *Int J Clean Coal Energy* 01: 35.
- [11] Yu Z, Fang S, Lin Y, et al. 2015 Investigation of Rice Straw Combustion by Using Thermogravimetric Analysis. *Energy Procedia* **75** 144–149.
- [12] Wang G, Zhang J, Shao J, et al. 2014 Thermogravimetric Analysis of Coal Char Combustion Kinetics. *J Iron Steel Res Int* **21** 897–904.