

## Co-gasification kinetics of coal char and algae char under CO<sub>2</sub> atmosphere

Nasim M. N. Qadi<sup>a</sup>, Arif Hidayat<sup>b</sup>, Fumitake Takahashi<sup>a</sup> and Kunio Yoshikawa<sup>a</sup>

<sup>a</sup>Department of Environmental Science and Technology, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa, 226-8502, Japan; <sup>b</sup>Chemical Engineering Department, Faculty of Industrial Technology, University of Islam Indonesia, Jalan Kaliurang k. 14, 5 Slemen 55584, Indonesia

### ABSTRACT

In this study, Newlands coal char and spirulina algae char were prepared separately in a fixed bed reactor with a pyrolysis temperature of 1000 °C. The isothermal CO<sub>2</sub> co-gasification experiment was done using a thermogravimetric analyzer in the temperature range of 800–1000 °C. The volumetric model (VM), the shrinking core model (SCM), the random pore model (RPM) and the modified random pore model (MRPM) were applied to describe the gasification kinetics of the samples. The results show that synergetic effects were observed for all ratios while the 5:5 blend demonstrates the best performance which may be attributed to the high content of potassium included in the algae char which in turn promotes the catalytic effect. Among the above-mentioned models, RPM was found to be predicting the conversion profile best among all tested models except for the algae sample which failed to fit the data by RPM and hence MRPM was applied for the algae sample only. RPM and MRPM were adopted to calculate the kinetics parameters. The activation energy and the pre-exponential factor were determined using the Arrhenius equation. The activation energy for all chars was found to be in the range of 100–200 kJ/mol.

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## Introduction

Coal is an abundant and low cost fuel. However, greenhouse emissions are major concerns of coal direct firing. Shifting the focus on more environmentally friendly thermochemical technologies like gasification enables clean use of the abundant reserves of coal and helps to reduce the coal carbon footprint.

Coal gasification has been widely investigated. Results approved that high-rank coal is preferred for gasification, since lower energy than low-rank coal is needed to drive out the moisture and volatile matters [1]. However, high-rank coal has a lower reactivity than low-rank coal [2]. Although coal gasification is usually conducted in an air, steam or air–steam mixtures environment, it can also be done with CO<sub>2</sub>. Despite higher carbon monoxide production when CO<sub>2</sub> is introduced as a gasification agent, slow kinetics is the major drawback of CO<sub>2</sub> gasification [3]. The char–CO<sub>2</sub> reaction is often used to study different char reactivities since it is easy to measure [4]. Also, the char gasification step represents the reaction limiting phenomena in the thermochemical conversion process of biofuel [5]. However, in industrial applications, one of the common techniques used to enhance the gasification reactivity at a lower temperature is catalyst loading, taking into consideration the cost, the availability and the efficiency of the catalyst [6].

Mixtures of coal and biomass can be considered to be a potential fuel base for gasification and offer the advantage of a reduction in CO<sub>2</sub> emissions [7], and a net reduction of the CO<sub>2</sub> emission if CO<sub>2</sub> capture is incorporated as part of the process [8]. Furthermore, co-gasification technology can help to overcome obstacles that appear when individual coal or biomass is gasified and has the potential to create collaborative effects: (1) Thermal co-processing of coal with biomass may cause some synergetic interactions to take place leading to significant variation in the thermal reactivity of the fuels [9]; (2) The efficiency of coal gasification can be enhanced through the catalytic effect that comes from higher amounts of alkali and alkaline earth metals in biomass [10]; (3) Utilization of biomass with coal can help to overcome the limited availability of biomass due to its seasonal nature and so a stable supply of gasification materials can be guaranteed [7]; (4) The elevated co-gasification temperature assists to reduce tar formation from biomass, and helps to enhance the energy balance of coal gasification with lower temperature compared to coal-only gasification [11].

Land-based biomass, like sawdust, rice straw and cedar wood, have been widely investigated with coal co-gasification. Biofuel production from algae is expected to play an important role in securing energy supply in the next decade [12]. Algae is considered a

cost-competitive biofuel for the following reasons: faster growth, higher yield per area and higher CO<sub>2</sub> capture and photosynthesis [13]. Moreover, algae has high ash content which contains larger amounts of alkali and alkaline earth metals than most terrestrial biomass, thus better performance can be expected [14]. Drying the algae is the main technical drawback of algae utilization since it is a high energy consuming process [15]. However, various energy-efficient thermal drying technologies have been developed, including conventional heat recovery-based technologies [16]. Incorporation of a heat recovery process will help to mitigate the energy penalty of algae drying, and the drying effect becomes less influential when a limited amount of algae is used in the co-gasification process.

Many researchers have investigated the interaction behavior between coal and biomass during co-gasification process. Xu et al. [17] investigated co-gasification of three different coal rank samples with three different land-based biomasses, and reported a significant interaction, where a ratio of 1:4 of sawdust and lignite coal, respectively, showed the best synergetic effect. Jeong et al. [7] examined the co-gasification of the blended char of coal–biomass with CO<sub>2</sub>, and they found that the reactive synergy of the char is increased with increasing the biomass amount in the blend. Several gasification studies have been done on algae individually. Sanchez-Silva et al. [18] studied the steam gasification of *Nannochloropsis gaditana* microalgae by means of TGA-MS and found that hydrogen production is improved by steam gasification. Hognon et al. [19] compared the reactivity of steam gasification for microalgae and lignocellulosic biomass chars by means of TGA and reported that the inorganic contents of all samples dominate the reactivity profiles. The available studies about co-gasification of microalgae with other fuels are very scarce. Kaewpanha et al. [20] studied steam co-gasification of brown seaweed and land-based biomasses, and they found that higher gas yield was obtained when higher seaweed amounts than land-based biomass amounts were used because of higher alkali and alkaline species. Kirtania et al. [21] studied the effects of different pyrolysis conditions and heating rates on the CO<sub>2</sub> gasification kinetics of algal and woody char, and found that the activation energy is highly dependent on the biomass and pyrolysis conditions, and the reactivity varies significantly with the pyrolysis conditions of the chars. Zhu et al. [22] studied the co-gasification of Australian brown coal with algae in a fluidized bed reactor, and found that more syngas is produced and agglomeration problems appear when a high ash content algae specie is used. Alghurabie et al. [23] investigated the fluidized bed gasification of Kingston coal with 10 wt% of marine microalgae in a spouted bed reactor,

and they found the high salt content in the algae leads to operational problems such as agglomeration and fouling.

Although the thermogravimetric analysis of the co-combustion kinetics of the algae–coal blend has been reported by Tahmasebi et al. [24] and the co-pyrolysis kinetics of the algae–coal blend has been studied by Kirtania et al. [25], a thermogravimetric study of algae–coal blend co-gasification is missing from the literature.

In light of the unique properties of microalgae, especially the high ash content, this research targets to clarify the feasibility of co-processing of algae with coal in terms of: (1) The occurrence of inhibiting or catalytic effects when microalgae is co-gasified with coal; and (2) To understand the reaction kinetics.

## Method

### Samples

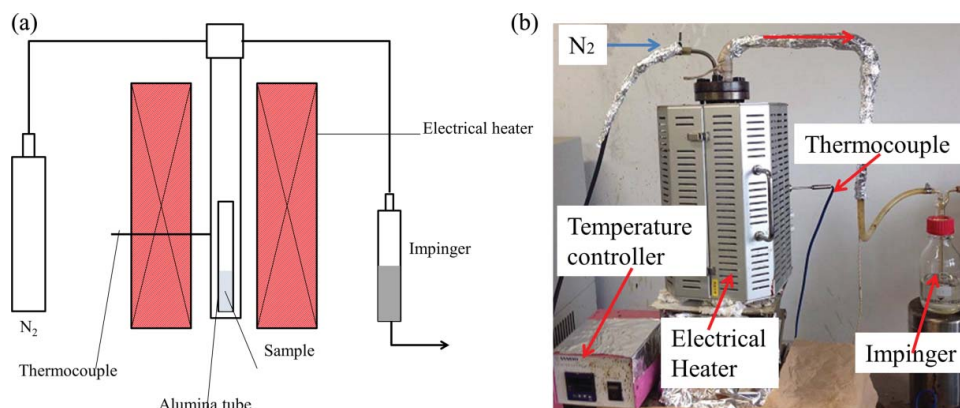
Spirulina algae (ALG) cultivated in a fresh water pond was supplied by Indonesia Islamic University. Newlands coal (NC) was imported from Australia by Central Research Institute of Electrical Power Industry (CRIEPI) in Japan. The proximate analysis experiment was performed for around 10 mg of each sample as follows: (1) before start heating up and under N<sub>2</sub> flow of 150 mL/min, hold for 10 min; (2) heat from room temperature to 110 °C at a temperature ramp rate of 20 °C/min, hold for 7 min; (3) heat from 110 to 900 °C at a ramp of 25 °C/min, hold for 5 min; (4) switch the gas from N<sub>2</sub> to air with the same flow, hold until no mass change is detected. Ash analysis was determined using a S2 Ranger energy dispersive X-ray fluorescence spectrometer (Bruker AXS, Germany). The proximate and ash analyses of these samples is given in Table 1.

### Char preparation

Coal and algae samples were kept in an oven at a temperature of 105 °C for 24 h. Figure 1(a) and (b) show the schematic diagram of the batch pyrolysis set-up and a photograph of the experimental facility, respectively, where a 6–8 g sample of each fuel was pyrolyzed

**Table 1.** The proximate and ash analysis results of the samples.

	Coal (wt%)	Algae (wt%)
Proximate analysis		
Volatile matter (V <sub>m,d</sub> )	28.70	79.25
Fixed carbon (C <sub>d</sub> )	57.50	7.69
Ash (A <sub>d</sub> )	13.80	13.06
Ash analysis		
SiO <sub>2</sub>	49.90	8.73
Fe <sub>2</sub> O <sub>3</sub>	4.40	2.88
CaO	1.78	9.42
MgO	0.72	6.47
SO <sub>3</sub>	0.77	18.80
P <sub>2</sub> O <sub>5</sub>	1.10	18.70
Na <sub>2</sub> O <sub>3</sub>	0.26	12.30
K <sub>2</sub> O	0.57	21.70



**Figure 1.** (a) Scheme of the fixed bed reactor for char preparation. (b) Photograph of the fixed bed reactor for char preparation.

in a fixed bed reactor equipped with alumina tube inside and an electrical heater was used to heat the reactor. A thermocouple was inserted into the heater to touch the outer surface of the reactor. The term ‘reactor temperature’ hereafter in this paper refers to the temperature that was read by the thermocouple. Before heating the set-up, the system was purged with nitrogen for 30 min to ensure an oxygen free environment inside. The sample residence time was 30 min at the final temperature of 1000 °C. Char was cooled to room temperature before opening the reactor. Nitrogen flow rate was kept constant at 200 mL/min during the pyrolysis experiment.

### Char gasification experiment

Char samples were crushed and sieved to a sample size of less than 100  $\mu\text{m}$ . The isothermal gasification experiment was conducted by a thermogravimetric analyzer (DTG-50, Shimadzu Inc.) in the temperature range of 800–950 °C for algae and in the range of 850–1000 °C for the blend with 50 wt% algae and 900–1000 °C for coal and blended samples with 30 wt% of algae. The final char sample weight was kept around  $4.7 \pm 0.2$  mg before injection of  $\text{CO}_2$ . The  $\text{CO}_2$  flow rate was around 200 mL/min for all experiments. Crucible height was kept as low as 2 mm to avoid the effect of the gas diffusion over a high wall [26]. In order to ensure reproducibility of data, each experiment was carried out at least twice.

### Methods of data analysis

#### Synergy analysis

TGA lists the sample weight values as a function of time. The experimental conversion ratio ( $X$ ) and the gasification rate ( $R$ ) were calculated according to Equations (1) and (2). The calculated conversion ratio ( $X_c$ ) which assumes there is no interaction between particles of coal char and algae char during co-gasification can be calculated according to Equation (3) [27]. The

extent of the synergetic effect ( $Syn$ ) can be evaluated by finding the difference between the experimental and calculated conversion ratios at the same temperature as shown in Equation (4) [28].

$$X = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (1)$$

$$R = \frac{dX}{dt} \quad (2)$$

$$X_c = \frac{v_c(m_{c0} - m_{ct}) + v_b(m_{b0} - m_{bt})}{v_c(m_{c0} - m_{c\infty}) + v_b(m_{b0} - m_{b\infty})} \quad (3)$$

$$Syn = X - X_c \quad (4)$$

$m_{c0}$ ,  $m_{ct}$  and  $m_{c\infty}$  represent the initial mass of coal char, the instantaneous mass of coal char at time  $t$  and the coal ash mass, respectively.  $m_{b0}$ ,  $m_{bt}$  and  $m_{b\infty}$  represent the initial mass of algae char, the instantaneous mass of algae char at time  $t$  and the algae ash mass, respectively.  $v_c$  and  $v_b$  refer to the coal char mass fraction and algae char mass fraction in the blend, respectively.

#### Kinetic analysis

The change in the apparent reaction rate is generally represented by Equation (5):

$$\frac{dX}{dt} = k(T, P_{\text{CO}_2})f(X) \quad (5)$$

Assuming that the partial pressure of  $\text{CO}_2$  remains constant during the gasification process, the reaction rate ( $k$ ) can be represented according to the Arrhenius equation as:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (6)$$

$A$ ,  $R$  and  $E$  are the pre-exponential factor, the universal gas constant (8.314 J/mol K), and the activation energy respectively. The function  $f(X)$  has a structural meaning and depends on the conversion. This function

can be expressed by many models which are based on assumptions. In this study, the following models were applied: the volumetric model (VM), the shrinking core model (SCM), the random pore model (RPM) and the modified random pore model (MRPM).

VM assumes homogenous reaction throughout the volume of the reactant particle [29,30] and is given by Equation (7):

$$\frac{dX}{dt} = k_{VM}(1 - X) \quad (7)$$

SCM assumes that the non-reacting core is at the center and the reaction takes place on the surface and gradually moves inside the particle [29,31–33]. The model is given by Equation (8):

$$\frac{dX}{dt} = k_{SCM}(1 - X)^{\frac{2}{3}} \quad (8)$$

Bhatia and Perlmutter proposed a complicated model called the random pore model (RPM), which incorporates the structural change during the gasification process. The RPM is given by Equation (9) [34]. RPM assumes the surface area increases due to the coalescence and overlapping of the pores. These changes are expressed by the structural parameter  $\Psi$  which depends on the surface area, the pore length and the solid porosity. Furthermore, the structural parameter can be calculated by finding the maximum conversion ratio  $X_{MAX}$  which occurs when the reactivity reaches its peak value as shown in Equation (10): [31].

$$\frac{dX}{dt} = k_{RPM}(1 - X)\sqrt{[1 - \Psi \ln(1 - X)]} \quad (9)$$

$$\Psi = \frac{2}{2\ln(1 - X_{MAX}) + 1} \quad (10)$$

The RPM model can predict the gasification behavior as long as the maximum gasification rate happens at the conversion ratio  $X < 0.393$ . Accordingly, Zhang et al. [35] proposed the modified random pore model (MRPM) which is indicated in Equation (11):

$$\frac{dX}{dt} = k_{RPM}(1 - X)\sqrt{[1 - \Psi \ln(1 - X)](1 + (1 + cX)^p)} \quad (11)$$

where  $p$  and  $c$  are dimensionless constants.

Table 2 summarizes the VM, SCM and RPM linearized solutions and the related rearranged forms of conversion equations.

## Results and discussion

### Sample characterization

The proximate and ash analysis results of both coal and algae samples are shown in Table 1. The proximate analysis was carried out by thermogravimetric analyzer (DTG-50, Shimadzu Inc.). The ash composition was analyzed by CHN analyzer.

Algae specie has higher volatile matter content, whereas coal has high fixed carbon content, which makes it high-rank coal. The ash content is high in both samples. However, the inorganic matter elements in both samples are quite different from each other. Alkali metals such as K and Ca are presented in a considerable amount in algae and are expected to accelerate the gasification rate by the catalytic action of char [35]. The coal sample contains large amount of Si which has been confirmed to have an inhibiting effect on the gasification reactivity [36].

### Co-gasification reactivity

Figure 2 shows the effect of the temperature on coal char gasification. It is clear that increasing the temperature shorten the gasification time and this is an expected result due to the fact that the Boudouard

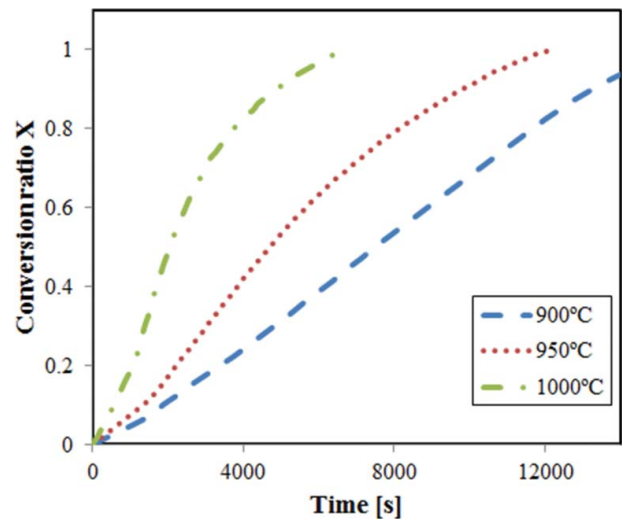
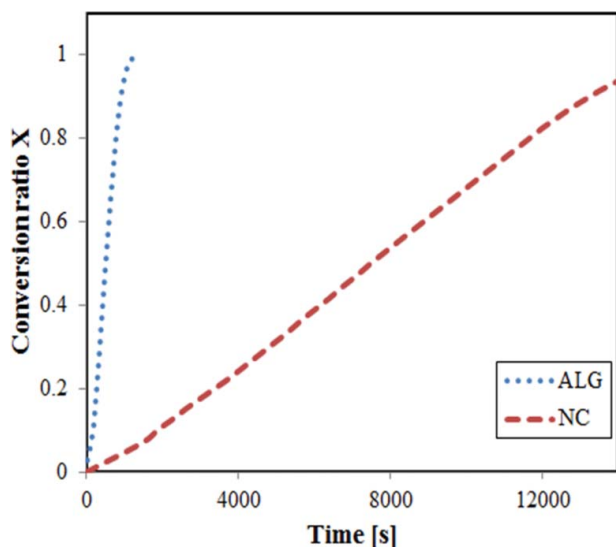


Figure 2. Effect of temperature on Newlands coal char gasification.

Table 2. The models linearized solutions and the related rearranged forms.

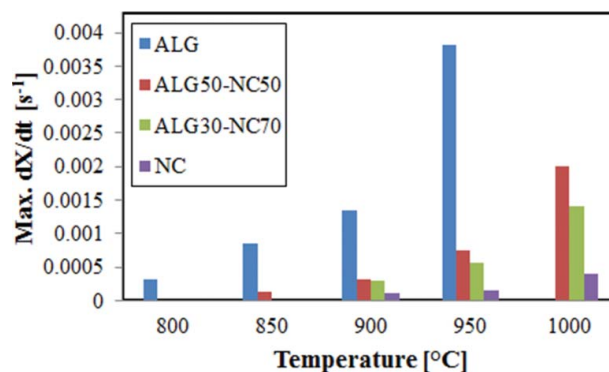
Model	Linearized solution	Conversion equation
VM	$-\ln(1 - X) = k_{VM} t$	$X = 1 - \exp(-k_{VM} t)$
SCM	$3 \left[ 1 - (1 - X)^{\frac{3}{2}} \right] = k_{SCM} t$	$X = 1 - \left( 1 - \frac{k_{SCM} t}{3} \right)^{\frac{2}{3}}$
RPM	$\frac{2}{\Psi} \left[ \sqrt{1 - \Psi \ln(1 - X)} - 1 \right] = k_{RPM} t$	$X = 1 - \exp\left(-k_{RPM} t \left( 1 + \frac{\Psi k_{RPM} t}{4} \right)\right)$



**Figure 3.** Effect of char type on gasification at 900°C.

reaction is an endothermic reaction. The conversion increases linearly from the beginning of the reaction until a conversion ratio of around 90% is reached. The reaction then proceeds very slowly until completion due to the collapsing of porous structure and the increasing resistance of ash layer for the reactant gas diffusion.

Figure 3 presents the carbon conversion ratio versus time of the char samples of coal and algae at 900°C. The time needed to reach the carbon conversion of  $X = 0.80$ , which is our characteristic conversion in this research, was about 12,000 seconds and 800 seconds for coal and algae char samples, respectively. This implies that the coal char gasification rate was 15 times slower than the algae char gasification rate. These differences could be attributed to the differences in alkali earth metals presented in both samples. The Si compound contained in the coal char have been confirmed to have deactivation effects. Also the P compound was reported to have similar deactivation effects like Si [37]. Both compounds Si and P were contained in large amounts in the coal sample. However, K compounds in the algae char sample are around 38 times higher than those in the coal char sample as shown in Table 1. One of the main mechanisms through which potassium catalyzes the reactivity of char gasification is to increase the number of active sites which in turn increases the oxygen concentration obtained from  $\text{CO}_2$  on the surface of carbon [38]. Other factors like a larger surface area, porosity and char preparation conditions may have contributed to a higher algae char gasification reactivity [39]. In light of the above, a considerable enhancement of the coal–algae char blend gasification reactivity is expected, especially if the algae char has the ability to adhere to the surface of the coal char so that the gasification of the coal char might be influenced by the catalytic effect of the residual minerals from the algae char after the algae char is gasified [39].



**Figure 4.** Comparison of the maximum reaction rate for the studied samples.

In this study, the co-gasification experiments were carried out for the blending ratios of 50 and 30 wt% of the algae char in order to investigate the effect of the blending ratio on the co-gasification reactivity. Furthermore, to ensure a pure chemically controlled reaction and to eliminate the pore diffusion effect on the evaluation of the calculated conversion ( $X_c$ ), the studied temperature ranges were set: for coal (NC) (900–1000°C), for algae (ALG) (800–950°C), for 50% blend (ALG50-NC50) (850–1000°C), and for 30% algae blend (ALG30-NC70) (900–1000°C). The theory behind the selected temperature ranges will be explained in the next section. Additionally, Kim et al. [40] confirmed that mass transfer (gas diffusion), which includes both the diffusion inside the coal char bed and inside the pores of the single particle, is negligible and the reaction is still chemically controlled if the maximum reaction rate doesn't exceed the value of  $0.0082 \text{ s}^{-1}$ .

Figure 4 presents the maximum reaction rate of gasification which was always less than  $0.004 \text{ s}^{-1}$  and the algae char sample had a maximum reaction rate at 950°C. In this study, the agreement between the two above-mentioned rules was adopted to decide the studied temperature ranges where the reaction is considered chemically controlled.

Figure 5(a) shows the experimental conversion ratio of the ALG50-NC50 blend at 900°C with the corresponding calculated conversion ratio ( $X_c$ ) which was determined by Equation (3). Initially, the calculated conversion ratio is larger than the experimental one until a value around 0.44, indicating that an inhibiting effect happened between the two chars and this may be attributed to the intimate contact between the algae char and the coal char. However, above the conversion ratio of 0.44, the experimental conversion ratio becomes larger than the calculated one, which implies a synergetic effect occurs through the catalytic effect of the alkali contents in algae ash on the coal char reactivity. A similar behavior about co-gasification of coal with terrestrial biomass has been reported by Ding et al. [41]. The time required for ALG50-NC50 to reach 0.80 conversion ratio was around 2850 s based on the

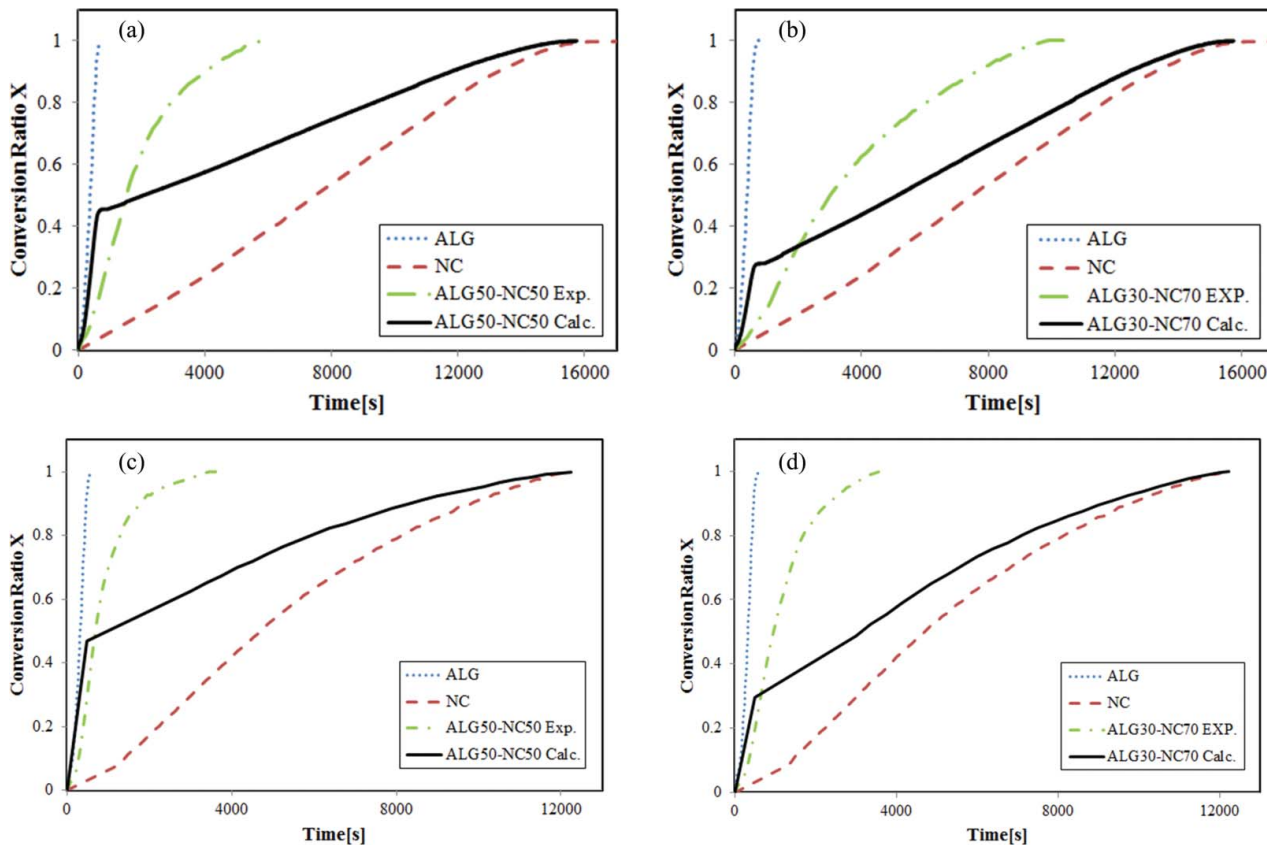


Figure 5. Experimental and calculated conversions for co-gasification experiment (a), (b) at 900°C and (c), (d) at 950°C.

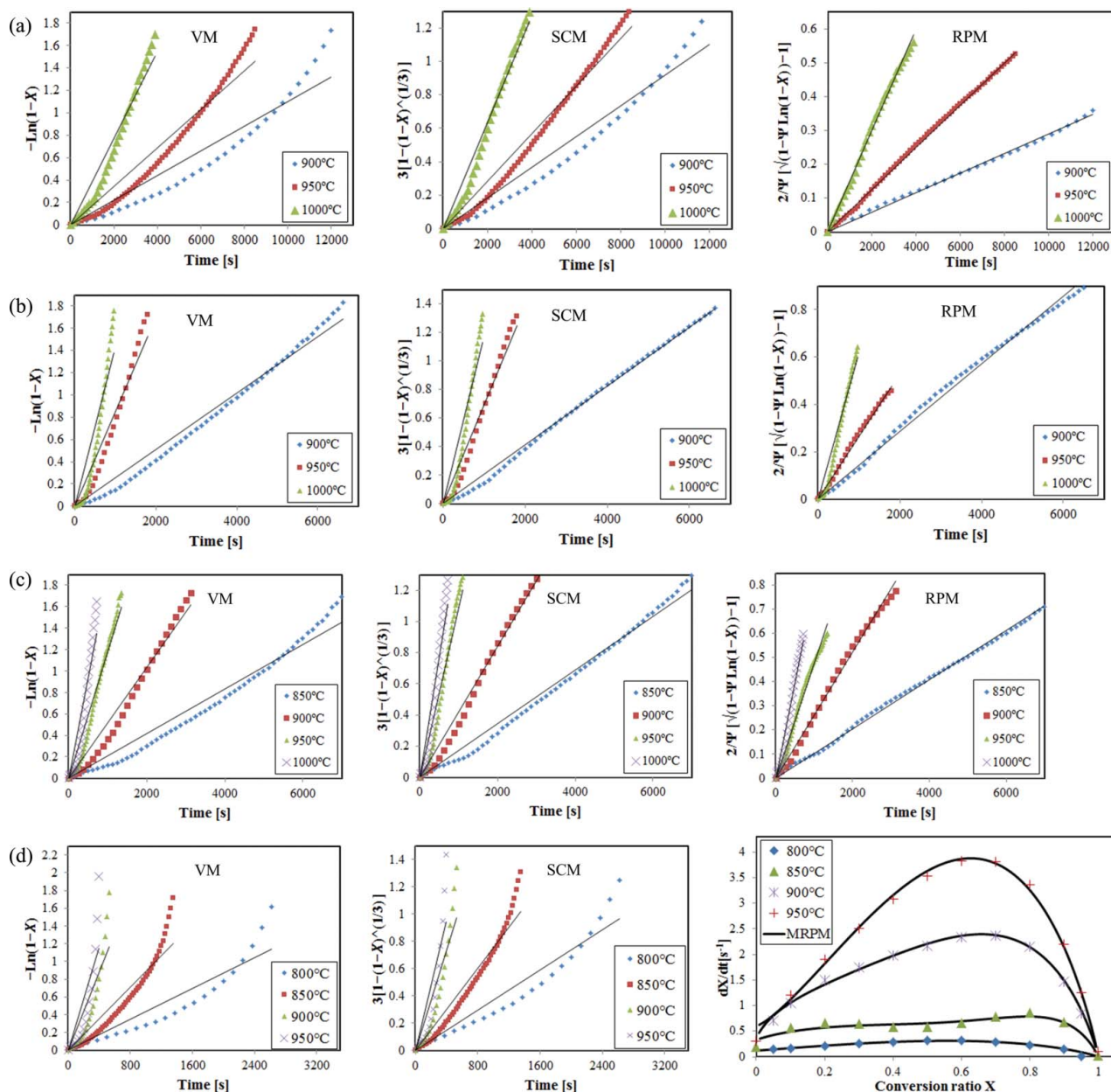
experimental run which is much shorter compared to the calculated time of 9000 s for the same conversion ratio. This means that an obvious catalytic effect happened which shortened the time to reach the conversion ratio of 0.80 by a factor of nearly 3.

In order to investigate the effect of the temperature on the reactivity behavior, gasification at 950°C was studied and the results showed that the inhibiting effect, which happened until  $X < 0.44$ , has been reduced with the increase of the temperature as shown in Figure 5(c) where the differences between the experimental and the calculated conversion ratio become smaller compared with the result shown in Figure 5(a). Moreover, the catalytic effect resulted in the experimental conversion ratio to be four times larger than the calculated one at the conversion ratio of 0.80. This may be explained by assuming that the fusion and dissolution of mineral matter in the algae char which catalyzes the coal char must take place to a larger extent at higher temperatures [42]. Figures 5(b) and (d) demonstrate the influence of the mixing ratio on the behavior of the co-gasification reactivity, where the ALG30-NC70 blend shows two distinct differences from the ALG50-NC50 blend. Firstly, a slower response at both studied temperatures implies that the synergetic effect is reduced when the blending ratio is reduced. Secondly, the inhibiting effect extends until less than 0.30 conversion ratio, beyond the conversion behavior is reversed and the catalytic effects were observed.

### Kinetic modeling

In order to explain the co-gasification reaction, the data indicating the carbon conversion ratio from  $X = 0$  to  $X = 0.80$  was used. The reason behind this is that a high conversion ratio, due to the collapsing of the actual porous structure characteristics, makes the ash layer resistance to dominate the process completion [43]. The linearized solutions of the models of VM, SCM and RPM were utilized to find the rate constant. MRPM was used to replace RPM after it failed to be applied for ALG samples since the conversion rate exhibits its maximum value at the conversion ratio  $X \geq 0.393$ . MRPM was fitted to the data using the free source software SCILAB, on the basis of the nonlinear square method, a Levenberg–Marquardt algorithm (LMA) based function was applied to iterate the four-parameter problem of ALG samples. For the application of RPM, it was necessary to determine the pore structural parameter ( $\Psi$ ). In this study, the determination of  $\Psi$  was carried out according to Equation (10).

Figure 6 illustrates the application of the studied models used to fit the experimental data obtained at different temperatures for all coal–algae mixing ratios. Data analysis revealed that VM has the lowest values of the coefficient of determination ( $R^2$ ) followed by results of SCM. A better fitting can be observed for RPM and MRPM with higher ( $R^2$ ) values which lead to conclude the rate constant to be calculated by them. Table 3



**Figure 6.** Plots fitting of VM, SCM and RPM for (a) NC, (b) ALG30-NC70 and (c) ALG50-NC50 samples and VM, SCM and MRPM for (d) ALG sample.

**Table 3.** Kinetic and empirical parameters summary of the applied models.

Sample	T[°C]	VM		SCM		RPM / MRPM				
		k[s <sup>-1</sup> ]	R <sup>2</sup>	k[s <sup>-1</sup> ]	R <sup>2</sup>	Ψ	c	b	k[s <sup>-1</sup> ]	R <sup>2</sup>
ALG	800	0.00035	0.8534	0.00037	0.9073	5.69	2.718	1.053	0.00012	0.9974
	850	0.0009	0.8979	0.00077	0.9406	16.27	3.779	4.853	0.0003	0.9176
	900	0.00164	0.8639	0.00136	0.9160	87.42	2.391	2.086	0.00036	0.9921
	950	0.0025	0.7525	0.0019	0.8000	1.34	19.03	1.310	0.0006	0.9920
NC	900	0.00011	0.9076	0.00009	0.9505	42.71	–	–	0.00003	0.9966
	950	0.00017	0.9243	0.00014	0.9638	17.59	–	–	0.00006	0.9985
	1000	0.00039	0.9267	0.00032	0.9647	14.44	–	–	0.00015	0.9970
ALG50-NC50	850	0.00021	0.9568	0.00017	0.9847	7.76	–	–	0.00011	0.9978
	900	0.00052	0.9498	0.00042	0.9798	6.35	–	–	0.00026	0.9957
	950	0.00118	0.9250	0.00097	0.9600	12.51	–	–	0.00047	0.9890
ALG30-NC70	1000	0.00186	0.8214	0.00154	0.8785	28.50	–	–	0.00064	0.9600
	900	0.00025	0.9386	0.00021	0.9725	4.43	–	–	0.00014	0.9940
	950	0.00085	0.9115	0.00069	0.9534	24.31	–	–	0.00027	0.9957
	1000	0.00141	0.8013	0.00116	0.8649	10.86	–	–	0.00061	0.9515

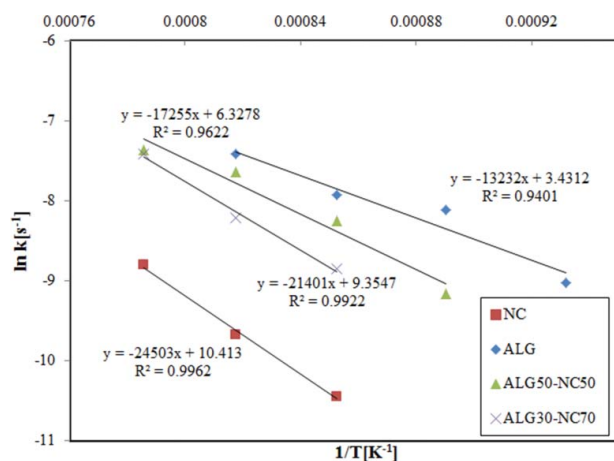


Figure 7. Arrhenius plot of the studied samples.

Table 4. Kinetic parameters.

Sample	$E_a$ [kJ mol <sup>-1</sup> ]	$A$ [s <sup>-1</sup> ]	$R^2$
ALG	110.01	30.94	0.9401
ALG50-NC50	143.46	559.92	0.9622
ALG30-NC30	177.93	11553	0.9922
NC	203.72	31404.3	0.9962

includes all fitting parameters and the coefficient of determination ( $R^2$ ) for the applied models.

In order to calculate the kinetic parameters, the Arrhenius law shown in Equation (6) was adopted. The relationship between the absolute temperature's reciprocal ( $1/T$ ) and the logarithm of the rate constant ( $\ln K$ ) was obtained for each model in the studied temperature range. A satisfactory linear relationship was noticed as shown in Figure 7. However, no obvious change in the line trend was observed in the studied temperature range. Therefore, the char gasification reaction is considered under the chemical reaction control. On the basis of the slope and the intersections values, the two kinetic parameters, the activation energy ( $E_a$ ) and the frequency factor ( $A$ ), were obtained for all studied models. These data are included in Table 4.

As shown in Table 4, the activation energy, which refers to the lowest temperature where the reaction can begin, varied significantly for all coal–algae blends. The coal sample exhibited the highest activation energy value and this value decreased as the percentage of algae increased in the blend. Thus, a catalytic effect was confirmed in terms of the activation energy reduction. Similar results were observed by other researchers for co-gasification of coal and terrestrial biomass, for example, Ding et al. [41] and Jeong et al. [7].

## Conclusions

Co-gasification of coal char and microalgae char was conducted in TGA under  $\text{CO}_2$  atmosphere. The synergistic effect was confirmed for all blends and the reaction time shortened by a factor of nearly 3 times at  $900^\circ\text{C}$  and 4 times at  $950^\circ\text{C}$  as in 50 wt% of algae

blend, and it has been found that the synergistic effects to decrease with the reduction of the algae weight ratio as in 30 wt% of algae blend. The catalytic effect may be attributed to the high potassium content in algae char. Kinetics modeling were conducted for conversion ratios between  $X = 0$  and  $X = 0.80$ . RPM and MRPM have  $R^2$  values around 0.99 for most cases which are higher than other models. Consequently, the kinetics parameters were calculated by them. The modeling results established good information for gasifier design purpose.

This work is the first step to understand the co-gasification process of coal–algae blends. In the next step: a lab scale co-combustion experiment will be conducted in order to investigate the effect on syngas composition and tar formation.

## Acknowledgments

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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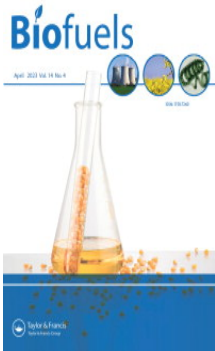
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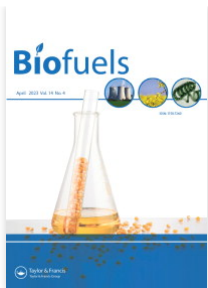
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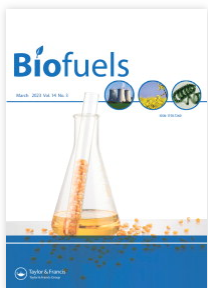
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