

Investigation of Co-Gasification Reactivity of Torrefied Jatropha Seed Cake with Illinois #6 Coal Char

Yuhong Qin,^{a,*} Zibing Zhao,^a Tomasz Wiltowski,^{a,b,*} Mashal Aloqaili,^b and Yanna Liang^c

Coal and torrefied biomass co-gasification is one of the potential solutions to the reduction of greenhouse gas emissions. For this study, Jatropha seed cake was torrefied at a temperature range of 200 to 300 °C under a nitrogen atmosphere. The torrefied material was then co-pyrolyzed and isothermally co-gasified at 900 °C with two Illinois (IL) #6 coal chars in a fixed-bed reactor connected to an on-line gas chromatography analyzer. Carbon dioxide and carbon monoxide were the primary gas products from the torrefaction process. Kinetic models, such as the shrinking core model, the homogenous model, and the catalysis-controlled model, were used to analyze the gasification mechanism. The results showed that the shrinking core and homogenous models provided the best fits for the gasification reaction data. Jatropha seed cake torrefied at 260 and 280 °C exhibited the best reaction activity with the IL #6 coal chars. The reactivities of coal char with torrefied biomass obtained at 200 and 300 °C were lower in comparison with the others.

Keywords: Jatropha seed cake; Torrefaction; IL #6 coal char; Co-gasification; Reactivity

Contact information: a: College of Chemistry and Chemical Engineering, Taiyuan University of Technology, No. 79 Yingze West Street, Taiyuan 030024, P. R. China; b: Advanced Coal and Energy Research Center, Southern Illinois University Carbondale, 405 West Grand Avenue, Carbondale, IL, 62901, USA; c: Department of Civil and Environmental Engineering, Southern Illinois University Carbondale, 1230 Lincoln Dr., Carbondale, IL, 62901, USA;

* Corresponding authors: qinyuhong@tyut.edu.cn; tomek@siu.edu

INTRODUCTION

Coal and biomass co-gasification is a promising technology for reducing greenhouse emissions and promoting the effective use of renewable biomass resources. From a technical perspective, the co-gasification process creates a beneficial scenario because coal and biomass have complementary elemental compositions. The high temperature of a coal gasifier can crack the biomass tar. At the same time, the high alkali metal content and active hydrogen and hydroxyl radicals in biomass can catalyze the coal gasification process (Howaniec *et al.* 2011; Kreckkaiwan *et al.* 2013; Tchabda and Pisupati 2014). For commercial operations, co-gasification technology could be successfully performed in an integrated gasification combined cycle system (IGCC), producing chemicals and transportation fuels (Rohan 2009; Sofia *et al.* 2014). However, several challenges still remain. First, the advantage of CO₂ reduction using biomass can be offset by CO₂ emitted during collection and transportation because of the low density and highly seasonal and dispersive characteristics of biomass. Second, because of its fibrous nature, the ratio of biomass should be below 20 wt.% to prevent blockages of the feeding setup. Third, the grinding of biomass requires a separate miller, which increases the operation costs (Dai *et al.* 2008; Barletta *et al.* 2013; Emami-Taba *et al.* 2013).

The torrefaction of biomass is a mild form of pyrolysis at temperatures ranging from 200 to 300 °C in an inert or limited oxygen environment (Basu 2014). The chemical composition of torrefied biomass is more homogeneous than that of raw biomass. Torrefied biomass exhibits an improvement in energy density and grindability. In comparison with raw biomass, which has an energy density of 10 to 11 GJ/m³, the energy content of the torrefied biomass is approximately 18 to 20 GJ/m³, with the potential to reduce transportation costs by 40% to 50% (Chiang *et al.* 2012; Batidzirai *et al.* 2013; Nunes *et al.* 2014). Torrefied biomass can be pulverized with a coal grinder, which lowers the handling cost when co-processing with coal. Presently, the largest market for torrefied biomass is for co-firing with coal (Goldfarb and Liu 2013; Nunes *et al.* 2014). Co-gasification technology remains at the lab-scale stage (Deng *et al.* 2009; Chen *et al.* 2013). Moreover, for the effective design of a co-gasification gasifier for torrefied biomass and coal, more information is needed on the char gasification, which can be regarded as the rate controlling step during the gasification process.

Jatropha is a fast-growing and vigorous drought- and pest-tolerant plant that can grow on barren and eroded lands. It prefers alkaline soils under harsh climatic conditions and is primarily cultivated in South Asia, India, Central and South America, and Africa (Khalil *et al.* 2013). It is named “diesel tree” or “petroleum tree,” as biodiesel can be produced from the oil extracted from its seeds. The Jatropha seed cake is the residue left after oil extraction. It is approximately 50% of the weight of the seeds, regardless of the oil extraction method (Liang *et al.* 2010). The seed cake is high in potassium, which is absorbed during Jatropha growth. This cake can be utilized as a feedstock for a small decentralized gasification or combustion plant (Singh *et al.* 2008; Christodoulou *et al.* 2014). Results from preliminary experiments show that the raw Jatropha seed cake is difficult to co-gasify with either raw coal or coal char under a steam environment in a fixed-bed reactor (Strege *et al.* 2011). The agglomeration of potassium may prevent the gasification reaction from occurring (Fryda *et al.* 2008; Doshi *et al.* 2014). Based on previous knowledge of torrefied biomass and coal co-gasification, the present study aims to investigate the thermal degradation characteristics and gasification mechanism of torrefied Jatropha seed cake blended with coal chars.

In this study, two coal chars with different residence times were prepared. The Jatropha seed cake was torrefied at temperatures ranging from 200 to 300 °C. When the desired temperature was reached, the samples were maintained at this temperature for 30 min. Two coal chars with different torrefied biomass mixtures were subjected to pyrolysis followed by isothermal gasification under a steam environment at 900 °C using a tubular reactor. Different kinetic models were optimized for different mixtures. The data obtained can be applied to the effective design and operation of a gasifier.

EXPERIMENTAL

Raw Material and Reactor

Illinois (IL) #6 coal was provided by the Knight Hawk Coal Co., LLC, Percy Township, IL, and the Jatropha seed cake was provided by the Ag-oil, Inc., LLC, Boca Raton, FL. The samples were ground and sieved to sizes below 500 µm. The results of proximate and ultimate analyses of these two raw materials are listed in Table 1. The proximate analysis followed the Chinese standard methodology GB/T 212-2008 (2009), and the ultimate analysis data was obtained from a Vario EL I elemental analyzer

(Elementar Analysensysteme GmbH, Germany). The ash chemical composition analyses are listed in Table 2. The test method for the analysis of these two samples followed the Chinese standard methodology GB/T 1574-2007 (2008). The standard methodology defines the repeatability and reproducibility limits for every element. For example, the repeatability and reproducibility limits for potassium oxide are 0.20% and 0.30%, respectively.

Table 1. Proximate and Ultimate Analyses of Coal and Jatropha Seed Cake

Sample	Proximate analysis (ad.**., wt.%)			Ultimate analysis (ad.**., wt.%)				
	Moisture	Volatile	Ash	C	H	O*	N	S
IL #6 coal	5.16	37.00	10.30	64.23	4.29	11.43	1.21	3.38
Jatropha seed cake	13.00	64.52	7.13	45.29	5.79	23.92	4.77	0.10

*by difference **ad.: air-dried basis

Table 2. Ash Constituent Analysis of IL#6 Coal and Jatropha Seed Cake (ad., wt.%)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅
IL #6 coal	39.45	16.41	11.55	15.34	0.47	1.71	11.35	1.19	0.74	1.10
Jatropha seed cake	5.06	35.17	0.43	4.43	17.55	4.10	2.05	23.20	2.95	4.63

Jatropha seed cake torrefaction, IL #6 coal pyrolysis and co-gasification experiments were performed in a tubular quartz tube reactor. A schematic diagram of the experimental equipment is shown in Fig. 1.

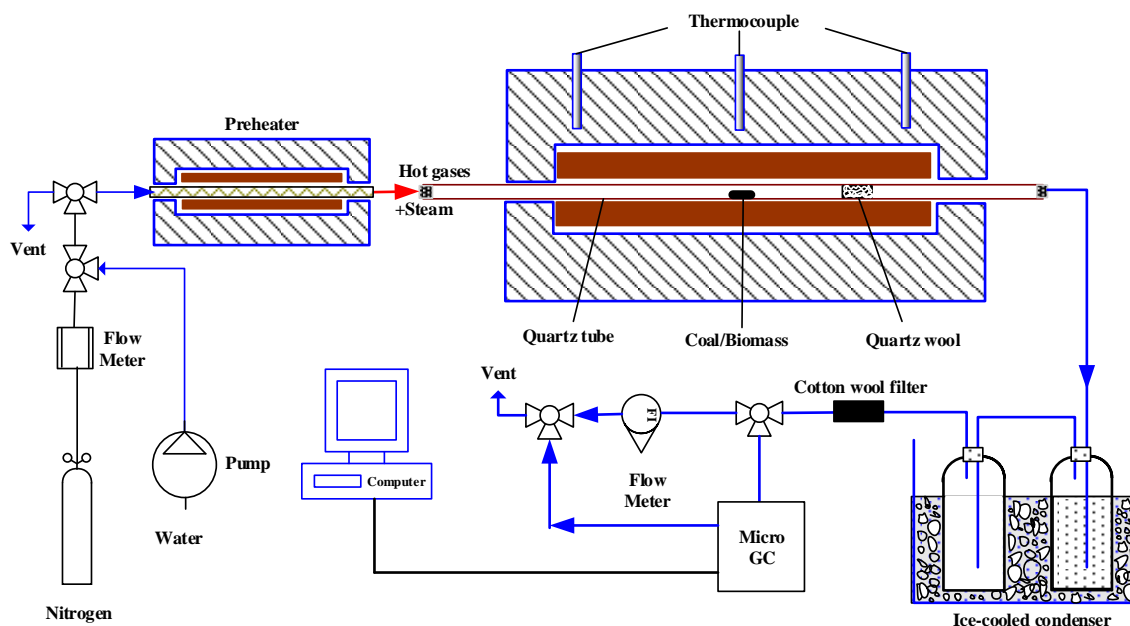


Fig. 1. Schematic diagram of the experimental setup

The fused quartz tubing size was 10.5 (I.D.) × 12.75 (O.D.) × 1200 mm (L). The tube furnace had three zones, and the samples were typically spread in the center zone. The quartz wool was dispensed into one end of the quartz tube to prevent the sample from blowing out. During the gasification experiment, deionized water at 0.02 mL/min was

pumped and carried with the carrier gas nitrogen at 75 mL/min into the preheated oven with a temperature of 225 °C. The steam flow rate was kept constant at 25 mL/min for all tests. During the test, product gas was emitted from the reactor and entered into an ice-cooled condenser. The product gas was analyzed with the on-line Agilent Micro-GC 3000 (Agilent Technologies, Santa Clara, CA). The interval between the two injections was 3 min. The total volume of each component was calculated using the volume of nitrogen.

Preparation of Test Samples

Preparation of coal chars

Two different coal chars were prepared using the tubular reactor connected to the on-line gas chromatography (GC) machine. The raw coal was heated at a rate of 25 °C/min up to 900 °C under flowing nitrogen. The first coal char (CC0) was prepared by heating to 900 °C, and when the maximum hydrogen formation was observed, the process was stopped and the reactor was cooled to room temperature under nitrogen flow. The second char (CC1) was obtained by heating to 900 °C and holding for 1 h, during which no hydrogen was detected. The yields of CC0 and CC1 were 59.31% and 58.08%, respectively. The chars were characterized using a BET Quantachrome 2000 analyzer (Quantachrome Instruments, Boynton Beach, FL). The specific surface areas of CC0 and CC1 were 8.657 and 1.102 m²/g, respectively.

Preparation of torrefied biomass

The Jatropha seed cake was heated from 25 °C to the desired temperature with a rate of 10 °C/min under a nitrogen atmosphere. After a holding time of 30 min, the power was turned off and the reactor was gradually cooled to room temperature under the same nitrogen atmosphere. The set temperatures were 200, 220, 240, 260, 280, and 300 °C, and the samples were referred to as 200 TB, 220 TB, 240 TB, 260 TB, 280 TB, and 300 TB, respectively. The elemental analysis of samples is shown in Table 3. A Thermo Scientific Flash 2000 thermal analyzer was used for the tests (Thermo Fisher Scientific, Waltham, MA).

Table 3. Elemental Analysis of the Tested Samples

Sample	N _{ad} (wt.%)	C _{ad} (wt.%)	H _{ad} (wt.%)	S _{ad} (wt.%)
CC 0	1.23	71.81	0.54	2.08
CC 1	1.40	74.41	0.47	2.25
200 TB	5.97	50.48	5.75	0.34
220 TB	5.70	52.03	5.53	0.30
240 TB	6.36	54.26	5.24	0.26
260 TB	6.06	57.75	4.94	0.21
280 TB	5.87	58.72	4.66	0.19
300 TB	6.44	58.08	4.40	0.19

Gasification Experiments in a Fixed-Bed Reactor

To keep the same amount of inorganic constituents in the torrefied biomass, especially the content of potassium, the loading ratio of different mixtures was 1:4 (raw biomass: raw coal).

Several studies (Khazraie Shoulaifar *et al.* 2013; Liu *et al.* 2014; Saleh *et al.* 2014) have investigated the emission of inorganic elements during torrefaction from 200 to 300 °C and observed chlorine volatilization as methyl chloride. Most alkali metals, such as potassium and sodium, remain in torrefied biomass with variable distribution.

Steam gasification experiments were carried out at a constant temperature in a tubular furnace reactor. Different combinations of CC0 and CC1 with six types of torrefied biomass were investigated. In each gasification experiment, samples of mixed char and torrefied biomass were spread in the center zone of the quartz tube and heated at a rate of 25 °C/min in flowing nitrogen at 100 mL/min up to 900 °C. The samples were maintained under these conditions until no hydrogen was detected. After that, the flow of nitrogen was changed to 75 mL/min and a water pump was turned on to deliver steam at a rate of 25 mL/min. The gas products were detected using an on-line GC system. All of the experiments were performed under conditions controlled by chemical reactions. For preliminary experiments, the internal and external diffusion were excluded. The conversion of the feedstock was small within the time interval where this reactor could be regarded as a differential reactor. The carbon conversion was calculated using Eq. 1,

$$X = \frac{\sum_0^i V_i \times (\text{CO}_2 + \text{CO} + \text{CH}_4 + 2\text{C}_2\text{H}_m) \times 12}{22.4 \times W \times C} \times 100\% \quad (1)$$

where X is the carbon conversion (%), i is the sample number by on-line GC, V_i is the total gas volume in the standard state, CO_2 , CO , CH_4 , and C_2H_m , are the percent gas concentrations in the total gas flow (%) (C_2H_m refers to C_2H_2 , C_2H_4 , C_2H_6), W is the initial sample weight (g), and C is the carbon content of the samples (%), excluding ash and moisture.

RESULTS AND DISCUSSION

Torrefaction of Biomass

As shown in Fig. 2, increasing temperature resulted in a decrease in the solid yield and an increase in the total gas yield. During the torrefaction process, the *Jatropha* seed cake was dried and then cracked. It became brittle after torrefaction because of the disintegration of its structure and a decline in lignin and cellulose contents, which are responsible for the recalcitrant fiber nature. In the temperature range of 200 to 260 °C, a majority of the inter- and intra-molecular hydrogen C-C and C-O bonds formed condensable liquids and non-condensable gases, such as CO and CO₂.

Hemicellulose, with higher carboxyl content, accounted for the increase in CO₂ yield (Yang *et al.* 2007). Carbon monoxide is produced by the reaction between CO₂ and steam within the porous char surface of the biomass (Basu 2014). The solid yield decreased sharply, from 73.01% to 50.27%. The gas yields of CO₂ decreased, while CO increased with the torrefaction temperature increase.

At a higher temperature range (260 to 300 °C) an extensive amount of hemicelluloses decomposition took place. In addition, a small amount of lignin and cellulose began to devolatilize and carbonize. Approximately 60% of the initial mass of *Jatropha* seed cake was consumed at 300 °C. At this temperature range, the gas production rate was slower than that from the light torrefaction process below 260 °C.

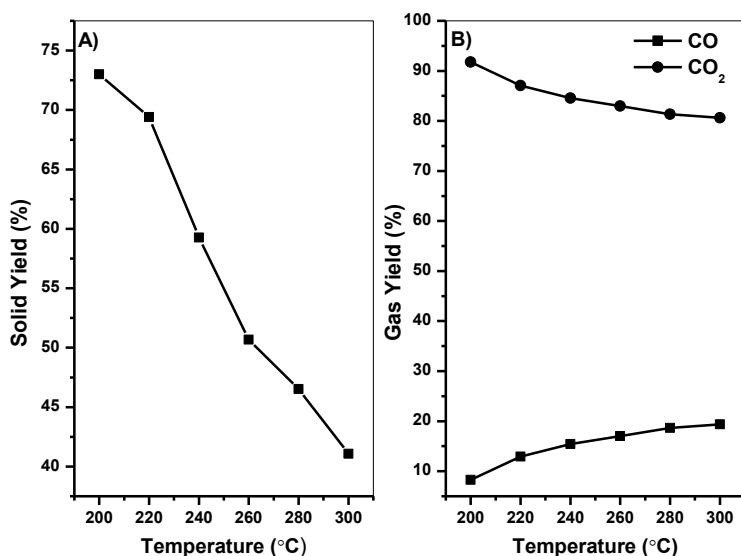


Fig. 2. The solids and gas yields during the Jatropha seed cake torrefaction process over a range of temperatures

Pyrolysis Behaviors of Various Feedstock Mixtures

The different gas yields of CC0 and CC1 with different torrefied biomasses during the co-pyrolysis process are shown in Fig. 3. CO and CO₂ were the primary gas products, and CO was more predominant than CO₂, with the exception of CC1 200 TB and CC1 220 TB. In addition, small amounts of H₂, CH₄, and C₂H₆ were detected. For CC1 and torrefied biomass mixture pyrolysis, the release of H₂ and CH₄ were attributed to the dissociation of torrefied biomass because there was no instantaneous yield of H₂ and CH₄ during the preparation of CC1. Hydrogen release occurs from the cracking of paraffins at higher temperatures due to the cellulose cracking and condensation (Chheda and Dumesic 2007; Qin *et al.* 2015). In another aspect, a higher presence of aromatic rings and methoxyls increases the cracking and deformation of lignin, releasing greater amounts of H₂ and CH₄ (Yang *et al.* 2007). The yield of CH₄ was similar for the different types of torrefied Jatropha seed cake.

The yields of CO and CO₂ decreased with the torrefied biomass preparation temperature. The formation of CO was primarily related to carbonyl and ether bond dissociations (Franco *et al.* 2003). Cellulose and hemicellulose are rich in hydroxyl groups that can transform into carbonyl-contained compounds through reforming and isomerization reactions (Yang *et al.* 2007). Ether bonds exist either between aromatic compounds or phenoxy compounds in lignin. In addition, the rate of the Boudouard reaction increased when the temperature was greater than 850 °C. The gas yield of CC0 and different types of torrefied biomass exhibited a slight increase compared to CC1 and different torrefied biomass. The maximum difference between CC0/torrefied biomass with CC1/torrefied biomass at same torrefied temperature for H₂, CO, CO₂, CH₄, C₂H₆ were 0.11 mMole, 0.07 mMole, 0.07 mMole, 0.02 mMole, and 0.003 mMole, respectively. It can be concluded that the yield of gas products was mostly contributed by torrefied biomass during various co-pyrolysis processes.

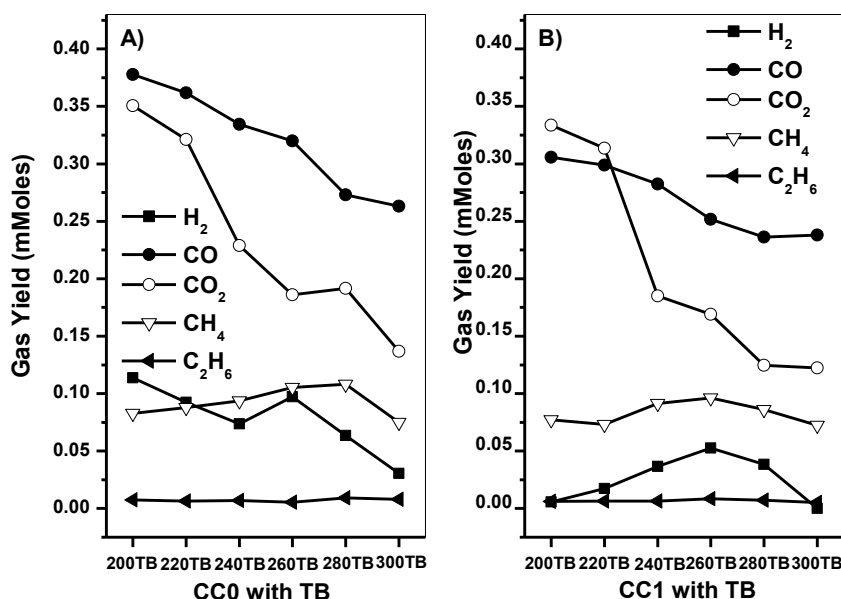


Fig. 3. Gas yield of CC0 or CC1 with different torrefied Jatropha seed cakes during the co-pyrolysis process

Carbon Conversion during Co-Pyrolysis and Co-Gasification

Carbon conversion for co-pyrolysis and co-gasification was calculated using Eq. 1 (Fig. 4). This graph clearly demonstrates that the carbon conversion was lower in co-pyrolysis than co-gasification. During the co-gasification process, CC0 200 TB and CC0 300 TB demonstrated lower reaction activity. The CC0 220 TB, CC0 240 TB, CC0 260 TB, and CC0 280 TB demonstrated similar gasification activity. The CC1 260 TB and CC1 280 TB were found to increase the gasification activity, while CC1 200 TB, CC1 220 TB, CC1 240 TB, and CC1 300 TB showed similar lower gasification activity.

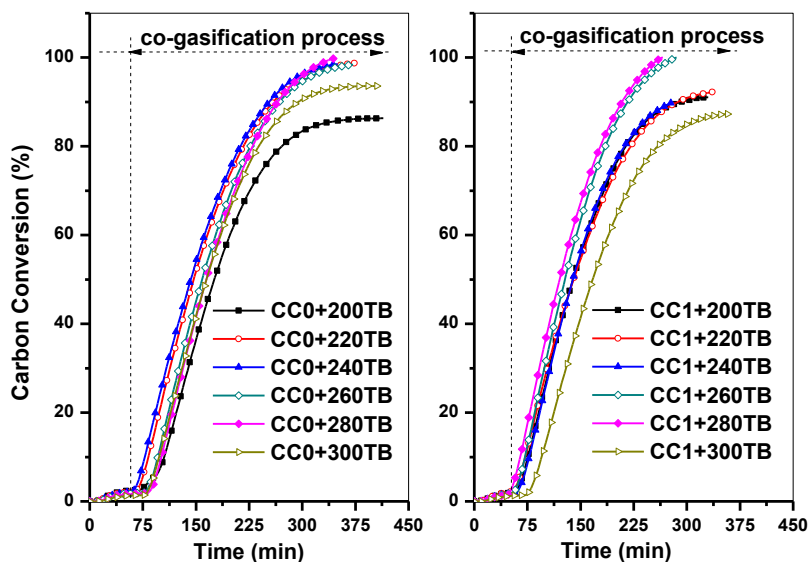


Fig. 4. Variation in the carbon conversion rate in response to heating time

It was obvious that the gasification activity of CC0 was better than that of CC1 because of the longer heating history, which increased the graphite content of coal chars. The active sites on the edge of aromatic nuclei decreased along with the length of the residence time (Radovic *et al.* 1983; Xu *et al.* 2013). Thus, it may be concluded that the mechanism of the gasification was associated with the composition of the material.

Kinetic Studies of the Co-Gasification Process

Various kinetic models have been proposed to describe the gas-solid reaction. The rate equation in a chemical-reaction-controlled regime can be expressed as,

$$\frac{dX}{dt} = k(1 - X)^n \quad (2)$$

where k is the kinetics reaction constant and X is the carbon conversion. Molina and Mondragón (1998) found that the homogeneous model ($n=1$) and the shrinking core model ($n=2/3$) are preferable for representing the conversion-time behavior of coal gasification. Moreover, because the *Jatropha* seed cake is rich in potassium, the gasification reaction may be controlled by catalytic action ($n=0$), *i.e.*, the catalysis-controlled model (Miura *et al.* 1986). The homogeneous model reduces the heterogeneous gas-solid reaction of coal gasification into a homogeneous reaction by assuming that the gas is reacting with char over the entire particle area. It should be noted that the particle size does not change during gasification; only the density of particles varies during the gasification process (Yuh and Wolf 1984; Wang *et al.* 2015). The reaction rate expression, after integration, is shown as follows:

$$X = 1 - \exp(-kt) \quad (3)$$

The shrinking core model (Lahijani *et al.* 2013) or unreacted core model (Ochoa *et al.* 2001; Wang *et al.* 2015) assume that the reaction initially occurs at the external surface of the char and gradually moves inside. During the intermediate conversion of a solid, the core of non-reacted solid shrinks. This reaction is described as follows:

$$\frac{dX}{dt} = k_{SCM} (1 - X)^{2/3} \quad (4)$$

After integration, Eq. 4 is modified to (Szekely and Evans 1970):

$$1 - (1 - X)^{1/3} = \frac{1}{3} k_{SCM} t \quad (5)$$

The catalysis-controlled model assumes that the gasification reaction is controlled by the presence of potassium in the biomass. The reaction is described as follows:

$$\frac{dX}{dt} = k_c, \quad X = k_c t \quad (6)$$

The validity of the above kinetic models was examined using the experimental results of all mixtures. Figure 5A shows the plot of $-\ln(1-X)$ over time for the homogeneous model. Figure 5B shows the plot of $1 - (1-X)^{1/3}$ over time for shrinking core model. Figure 5C shows the relation of conversion X and time (t) for the catalysis-controlled model. A linear equation was applied to each curve, and the slope indicated the rate constant, k . All of the rate constants (k) and corresponding regression coefficients (R^2) (Jeong *et al.* 2014)

of the curves are shown in Table 4. An examination of the plots concluded that the catalysis-controlled model was not the best fit for describing the torrefied biomass and the coal char co-gasification process. In addition, the catalysis effect of potassium in Jatropha seed cake was not important.

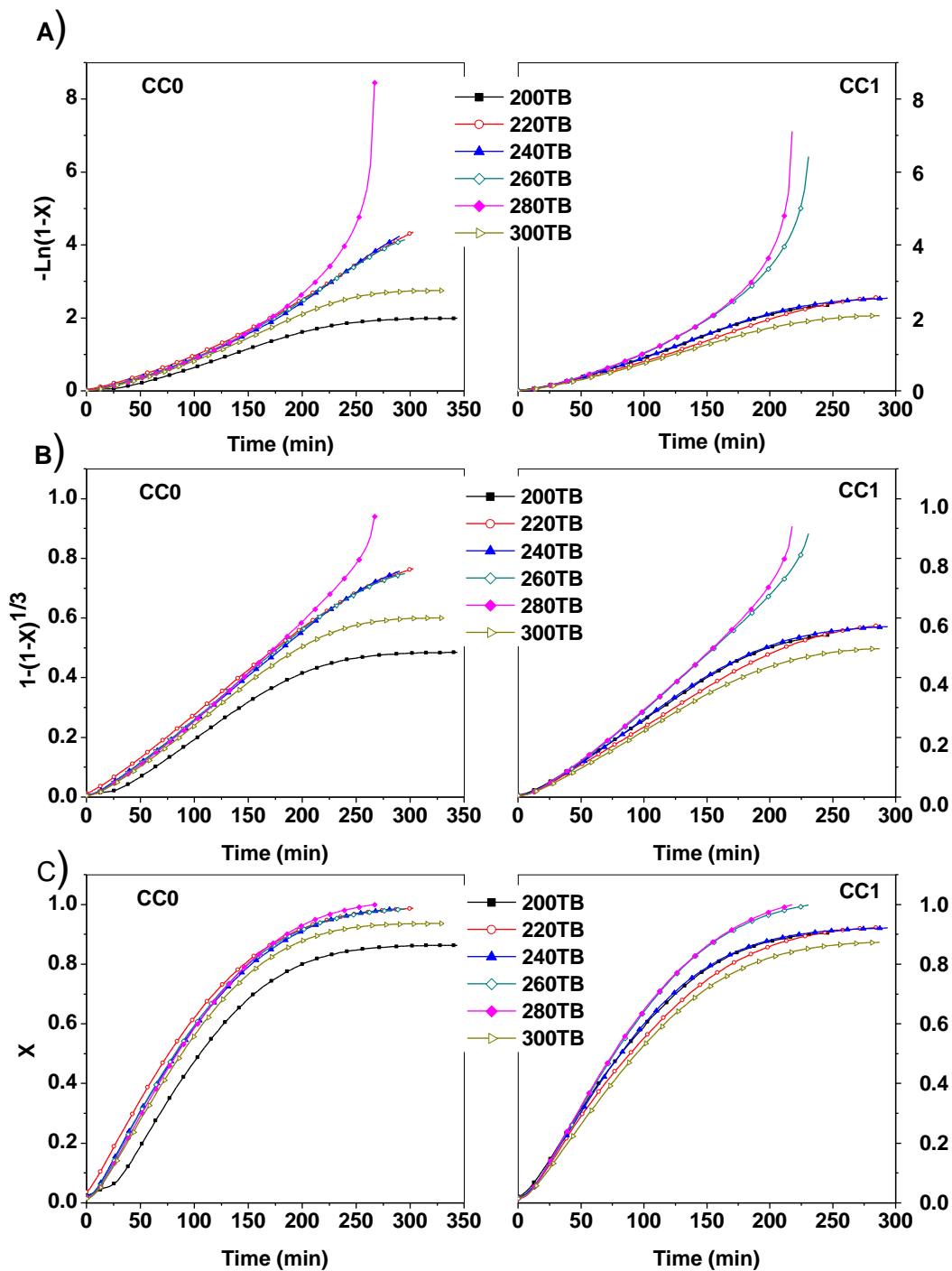


Fig. 5. Validity of three models for the gasification of coal char and torrefied Jatropha seed cake: (A) homogenous model; (B) shrinking core model; and (C) catalysis-controlled model

Table 4. Kinetic Parameters of Applied Models and Regression Coefficients

Sample	Homogenous model (n=1)		Shrinking core model (n=2/3)		Catalysis-controlled model (n=0)		Fitted model
	k_{HM}	R ²	$k_{SCM}/3$	R ²	k_C	R ²	
CC0							
200 TB	0.0069	0.9520	0.0016	0.9294	0.0026	0.8602	Homogenous model
220 TB	0.0149	0.9846	0.0027	0.9947	0.0031	0.8869	Shrinking core model
240 TB	0.0151	0.9741	0.0028	0.9978	0.0034	0.9118	Shrinking core model
260 TB	0.0149	0.9822	0.0028	0.9954	0.0034	0.9001	Shrinking core model
280 TB	0.0193	0.8399	0.0033	0.9908	0.0039	0.9389	Shrinking core model
300 TB	0.0099	0.9749	0.0021	0.9527	0.0028	0.8588	Homogenous model
CC1							
200 TB	0.0107	0.9934	0.0024	0.9860	0.0038	0.9267	Homogenous model
220 TB	0.0100	0.9935	0.0022	0.9831	0.0033	0.9104	Homogenous model
240 TB	0.0100	0.9805	0.0022	0.9578	0.0031	0.8697	Homogenous model
260 TB	0.0207	0.8839	0.0037	0.9907	0.0046	0.9441	Shrinking core model
280 TB	0.0211	0.8352	0.0038	0.9827	0.0049	0.9553	Shrinking core model
300 TB	0.0082	0.9837	0.0019	0.9666	0.0031	0.8990	Homogenous model

For the CC0 200 TB and CC0 300 TB co-gasification tests, the homogenous model gave the best fit for the experimental data; thus, the gasification reaction proceeded uniformly throughout the particles. For the CC0 220 TB, CC0 240 TB, CC0 260 TB, and CC0 280 TB co-gasification tests, the shrinking core model provided the best fit for the data. It was assumed that the gasification reaction began from external surface of the particles. On the other hand, the torrefied biomass gasification rate of CC1 260 TB and CC1 280 TB followed the shrinking core model. The others were better described by the homogenous model. The mixture comprising torrefied biomass with coal char at 220 TB and 240 TB exhibited higher regression coefficients (greater than 0.95) with the shrinking core and the homogenous models. A higher regression coefficient means that the model exhibits a better fit to the data it describes.

After further consideration of the carbon conversion and kinetic models, it was concluded that the mixtures following the shrinking core model exhibited a higher carbon conversion rate and that the torrefied biomass exhibited a synergy effect with the coal char. The mixtures following the homogenous model exhibited a lower carbon conversion rate, a greater number of reaction sites, and a faster gasification rate.

CONCLUSIONS

1. Two types of IL #6 coal chars and six torrefied Jatropha seed cakes were prepared over a range of processing temperatures. It was concluded that the catalytic effect of potassium in Jatropha seed cake was not a key factor in the mixtures. The shrinking core and homogenous models were the best fit for the gasification results.
2. Jatropha seed cake torrefied at 260 and 280 °C exhibited the best reaction activity with coal char, while the reactivities at 200 and 300 °C with torrefied biomass and coal char were lower in comparison with the others.

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