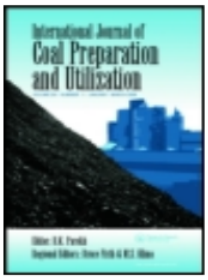
Kinetik Model 2020

by Anton Irawan

Submission date: 05-Apr-2023 02:09PM (UTC+0700)
Submission ID: 2056415942
File name: 2020_A_Kinetic_Model_Approach.pdf (2.33M)
Word count: 7445
Character count: 33161



Taylor & Francis
Taylor & Francis Group

International Journal of Coal Preparation and Utilization

ISSN: 1939-2699 (Print) 1939-2702 (Online) Journal homepage: https://www.tandfonline.com/loi/gcop20

A kinetic model approach for predicting coke reactivity index from coal and coal blend properties

Teguh Kurniawan, Anton Irawan, Hafid Alwan, Raden Hernanto, Wahyudi Wahyudi, Abdul Rozak Kodarif & Yazid Bindar

To cite this article: Teguh Kurniawan, Anton Irawan, Hafid Alwan, Raden Hernanto, Wahyudi Wahyudi, Abdul Rozak Kodarif & Yazid Bindar (2020): A kinetic model approach for predicting coke reactivity index from coal and coal blend properties, International Journal of Coal Preparation and Utilization, DOI: 10.1080/19392699.2019.1710498

To link to this article: https://doi.org/10.1080/19392699.2019.1710498

View supplementary material

Published online: 24 Jan 2020.

Submit your article to this journal

Article views: 34

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=gcop20

INTERNATIONAL JOURNAL OF COAL PREPARATION AND UTILIZATION
https://doi.org/10.1080/19392699.2019.1710498

Taylor & Francis
Taylor & Francis Group

Check for updates

A kinetic model approach for predicting coke reactivity index from coal and coal blend properties

Teguh Kurniawan[a,b], Anton Irawan[a,b], Hafid Alwan[a,b], Raden Hernanto[c], Wahyudi Wahyudi[c], Abdul Rozak Kodarif[c], and Yazid Bindar[b,d]

[a]Chemical Engineering Department, Sultan Ageng Tirtayasa University, Serang, Indonesia; [b]RT Aksiatama Foundation, Cilegon, Indonesia; [c]PT Krakatau Steel, Cilegon, Indonesia; [d]Institut Teknologi Bandung, Chemical Engineering, Bandung, Indonesia

ABSTRACT

A novel method has been developed to estimate coke reactivity index (CRI) from coal properties through a kinetic approach. The model was derived from mass balance with a kinetic model of batch reactor CRI test. The parameters of kinetic model were optimized using non-linear least squared method. Three main properties of coals, i.e., Fe_2O_3 content, volatile matter, and coal rank were selected to predict the CRI. The predicted CRI value was in a good agreement with the CRI data. The standard error was less than 5. Coke strength after reaction (CSR) was predicted using linear regression of the CSR and CRI data. The estimated CSR was in good agreement with the CSR data. The sensitivity analysis of coal properties to CRI was also performed using the developed kinetic model. The model was successfully applied for coal blending to predict CRI of the produced coke with standard error 3.7. This model can explain well the catalytic effect of coal and coal blend properties to coke reactivity during the CRI test.

ARTICLE HISTORY
Received 29 August 2019
Accepted 27 December 2019

KEYWORDS
Coal properties; coal blending; catalytic; kinetic model; CRI; CSR

Introduction

Coal is an important component in the blast furnace iron making, particularly in the form of coke. The role of coke in the blast furnace is (i) providing energy (ii) the main source of carbon monoxide and carbon for iron oxides reduction (iii) carburization the hot metal (iv) creating permeable support for the burden (v) acting as a gas distributor (Yang, Raipala, and Holappa 2014). Coke is prepared through high-temperature pyrolysis up to 1200°C in coke oven batteries. The hard-coking coal is well known as the best coal feedstock to produce coke. However, the hard-coking coal is expensive and scarce as compared to the low-rank coal. Blending the low-rank coal along with the hard-coking coal is a common practice in a blast furnace industry to reduce coke production cost.

The Indonesian Ministry of Energy and Mineral Resources reported that ca. 86.4% of Indonesian coal is categorized as low-rank coals such as lignite, bituminous and sub-bituminous (<6100 kcal/kg GAD basis) and only 1% anthracite type which is the hard coking coal (Stanford 2013) (Yustanti 2012). Blending the hard-coking coal with local low-rank coal could give benefit to the blast furnace producer. Recently, the biomass of

CONTACT Yazid Bindar ybybyb@fti.itb.ac.id Institut Teknologi Bandung, Chemical Engineering, Jl. Tamansari 64, Bandung 40116, Indonesia
Supplemental data for this article can be accessed here.
© 2020 Taylor & Francis Group, LLC

bamboo was also considered as feedstock to replace coal in the blast furnace as reported elsewhere (Song et al. 2018). Blending biomass charcoal produced from the carbonization of eucalyptus wood in Brazil with coking coal was also investigated (Flores et al. 2017). The authors reported that the coke quality was affected significantly by the blend composition and particle size of the charcoal. The charcoal increased the coke reactivity because of the large surface area created during the carbonization step.

Coke quality test is performed to ensure smooth operation of the blast furnace. Various coke quality tests are routinely practiced in industry. For examples are coke reactivity index (CRI) and coke strength after reaction (CSR). CRI test reaction is firstly introduced by Nippon Steel Corporation in 1970. The original purpose of CRI test was to simulate the decomposition process of coke under a pure CO_2 atmosphere to simulate gasification reactions in the blast furnace (Li et al. 2014). High CRI number indicating that the coke is easy to react with carbon dioxide. Typically, cokes with low CRI and high CSR are generally considered as a good quality for blast furnace operation.

The coke quality tests of CRI and CSR are often expensive and time consuming. Despite there is an attempt to test using a small scale setup to reduce the cost, it is still time consuming (MacPhee et al. 2013). Hence, it is important to estimate the coke quality from its coal parent properties using a model. Tiwari et.al developed a model based on composite coking potential to estimate CSR value (Tiwari, Banerjee, and Saxena 2013). Thermogravimetric analysis (TGA) for coke quality prediction was also reported elsewhere (Díaz-Faes et al., 2007). Recently, a review paper on model for coke quality prediction was discussed thoroughly by North et.al. (North et al. 2018). They concluded that there is no model that can globally suit for coke quality prediction.

CRI test is basically a gasification reaction performed in a semi-batch reactor. Hence, model of batch reactor model with a kinetic approach can be applied to predict the CRI. Early attempt study of predicting CRI using the kinetic approach was performed by Gyulmaliev et.al (Gyul'maliev et al. 2002). They studied the interrelationship between the indices of reactivity metallurgical cokes and CRI. However, the model was not incorporated its corresponding coal properties. To the best of our knowledge, there is no publication reported on kinetic model approach to estimate the CRI from its coal properties. Hence, the aim of this study was to develop a model based on kinetic and mass balance concept to predict the CRI from coal properties.

Model Development

Coke reactivity index (CRI) is tested according to standard procedure of ASTM D 5341. Carbon dioxide flows into the semi-batch reactor chamber filled with a 200 g coke sample at a constant temperature of 1100°C for 2 h (Fig. 1). CRI defined as the percentage of coke weight loss. Once the mole of coke at the end of reaction determined, one may convert the mole into mass and calculated the CRI according to Equation 1.

$$CRI = \frac{200\ \text{g} - m(\text{g})}{200\ \text{g}} * 100\% \tag{1}$$

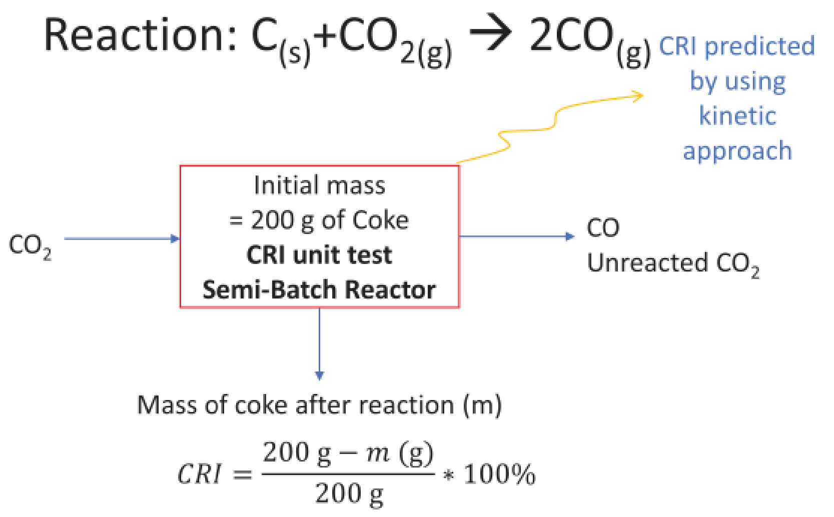


Figure 1. Coke reactivity index (CRI) analysis procedure at temperature 1100°C and time 2 h reaction.

The flow chart of modeling and simulation CRI based on kinetic approach is presented in Fig. 2. Model was developed based on the mass conservation and kinetic concept in a semi-batch reactor of CRI test device (Fig. 3). First-order reaction was taken for the coke reaction rate.

$$\text{Coke accumulation} = \text{Coke in} - \text{Coke out} + \text{Reaction rate} \tag{2}$$

$$\frac{dn_c}{dt} = 0 - 0 - k\rho_c S_a n_c \tag{3}$$

$$\frac{dn_c}{dt} = -k\rho_c S_a n_c \tag{4}$$

$$\frac{dn_c}{dt} = -k' n_c \tag{5}$$

where n_c is coke amount in mole, k' is rate of reaction constant in 1/s, k is Arrhenius constant of reaction rate in m/s, ρ_c is coke density in kg/m^3, S_a is coke surface area in m^2/kg.

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

where A is pre-exponential factor in m/s, Ea is activation energy in J/mole, R is gas constant in J/(mole.K) and T is temperature in Kelvin.

Coal properties were selected based on linear regression of each coal properties, i.e. Fe_2O_3, volatile matter (VM), reflectance vitrinite ($R_{v,max}$), SiO_2, TiO_2, K_2O, CaO, Na_2O, and Al_2O_3 percentage content in dry ash. The three most influencing properties on CRI shown by R^2

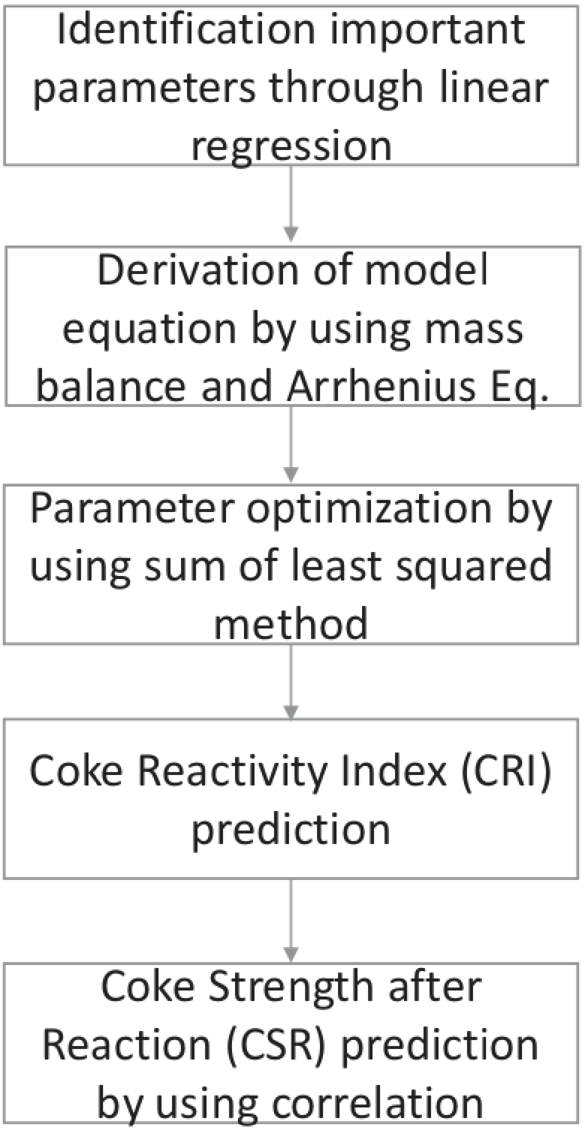


Figure 2. Flow chart of prediction CRI based on kinetic approach.

were chosen. The selected coal properties were incorporated within the kinetic equation to predict CRI of produced coke. Activation energy and pre-exponential parameters were optimized using the non-linear sum of least square method in MATLAB (Equation 7). Coke strength after reaction (CSR) was reported has a strong linear relation with CRI (Nag et al. 2009; Pusz and Buszko 2012; Ulanovskiy 2014; Wang et al. 2016). Hence, linear regression was performed to produce equation to predict CSR from CRI.

$$SSE = \sum \left(CRI_{predicted} - CRI\right)^2 \tag{7}$$

where SSE is sum of squared error and $CRI_{predicted}$ is CRI obtained from the kinetic model.

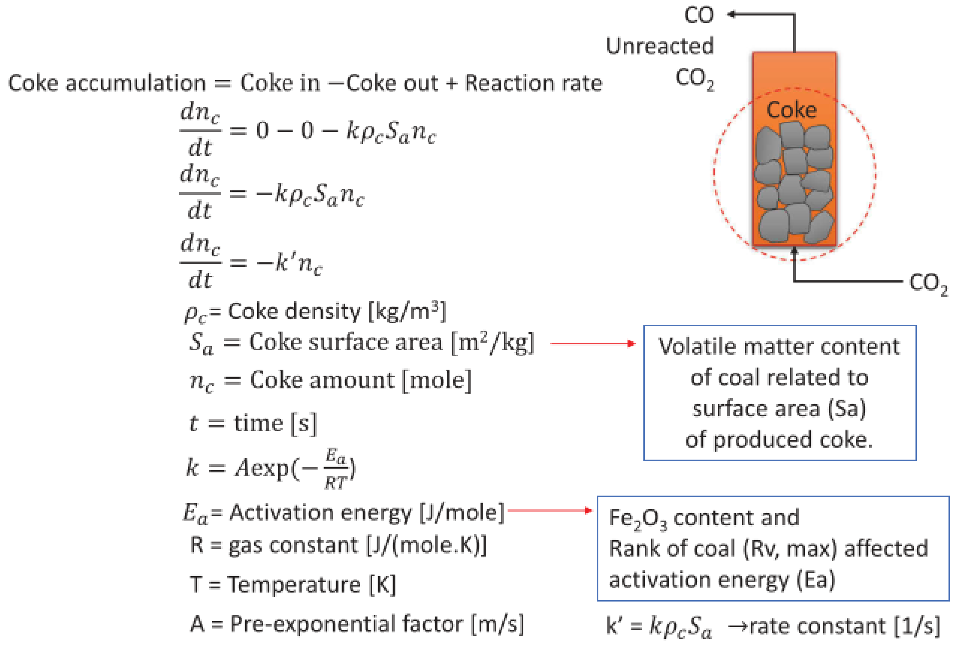


Figure 3. CRI prediction by using Arrhenius equation in a batch reactor.

Model Validation

A number of coal from various types (20 coal) i.e. hard-coking coal, semi-hard coking coal, semi-soft coking coal, were used to validate the CRI model (Table 1). Coal sample is labeled with Coal-1 until Coal-20 which was listed from the hard-coking coal to semi-soft coking coal. The CRI and CSR data were obtained from laboratory testing following the ASTM D 5341. The CRI and CSR data were compared with the CRI and CSR predicted. Standard error (S) was calculated using Equation 8 to evaluate the accuracy of model.

$$S = \sqrt{\frac{\sum \left(CRI_{predicted} - CRI\right)^2}{n-2}} \tag{8}$$

where n is the number of data sample incorporated in the calculation.

The model was also applied for predicting CRI from 18 coal blends of 5 different coals which was taken from daily operating coke oven batteries data. The coal blend properties, i.e., iron oxide content, volatile matter, and reflectance vitrinite were calculated using the additive law from its corresponding individual coal constituent as presented in Table 2. Furthermore, the kinetic model was applied for estimating CRI from 19 coal blends of 10 different coals which was taken from literature (Pusz and Buszko 2012). The predicted CRI of coal blends were compared with the corresponding CRI of coal blends data.

Table 1. Properties of coal and CRI coke produced.

Coal ID	Coal Type	Vm [%]	Rv, max [%]	Fe_2O_3 [%]	TiO_2 [%]	SiO_2 [%]	Na_2O [%]	Al_2O_3 [%]	K_2O [%]	CaO [%]	CRI [%]
Coal-1	HCC*	20.2	1.44	5.55	1.63	52.8	0.63	32.7	0.85	2.41	21
Coal-2	HCC	17	1.64	7.44	1.46	48.8	0.84	30.8	1.14	5.51	24
Coal-3	HCC	20.9	1.27	7.23	1.47	54.5	0.69	28.7	0.67	2.79	27
Coal-4	HCC	20.9	1.44	3.2	2.5	57	0.1	26	1.6	33	15
Coal-5	HCC	21.4	1.45	6.1	2.1	50.3	0.96	33.2	0.98	2.7	16
Coal-6	HCC	21.5	1.3	2.1	1.89	57.4	0.36	33.8	0.82	2	22
Coal-7	HCC	20.5	1.44	3.7	1.4	65.2	0.5	24.7	1	1.3	19
Coal-8	HCC	23.78	1.108	5.9	1	60.8	0.4	18.7	0.8	4.1	21.9
Coal-9	HCC	23.2	1.2	3.5	1.8	58.7	0.4	32.4	0.9	0.8	22
Coal-10	HCC	23.3	1.18	5.16	1.65	53.9	0.59	34.2	0.53	1.34	22
Coal-11	HCC	23.8	1.28	2.78	2.4	59.8	0.1	26.8	1.58	2.74	15
Coal-12	HCC	22.5	1.22	4.3	1.5	47.2	0.95	38.2	1.1	3	22
Coal-13	SHCC**	24.5	1.19	3.88	1.24	55.6	0.54	25.6	0.87	4.11	28
Coal-14	SHCC	29	1.27	8.25	1.2	55.4	2.31	25.4	1.57	2.12	26.4
Coal-15	SHCC	27.5	1.04	4.5	1.4	53	0.4	33	1.1	2.9	24
Coal-16	SHCC	27.5	1	8.87	0.12	53.6	0.58	25.4	1.4	3.3	39
Coal-17	SHCC	26.81	1.25	12.37	1.16	42.46	0.31	27.35	3.32	6.09	44.5
Coal-18	SSCC***	38	0.76	6.07	1.62	53.09	1.57	32	0.77	2.24	46.2
Coal-19	SSCC	34.8	0.79	4.62	2.58	50.65	0.69	37.31	0.21	0.35	31.7
Coal-20	SSCC	24.4	1.11	9.4	1.6	47.9	0.2	30.8	0.8	4.3	41
Coal-21	SSCC	39	0.74	8.25	-	-	-	-	-	-	-

*HCC = Hard Coking Coal
**SHCC = Semi Hard Coking Coal
***SSCC = Semi Soft Coking Coal

Table 2. Coal blending composition and coal blend properties.

Blending No.	Coal-1 [%]	Coal-10 [%]	Coal-18 [%]	Coal-19 [%]	Coal-21 [%]	Fe_2O_3 [%-ash]	Rv [%]	VM [%]	CRI [%]
1	15	60	25	0	0	5.4	1.1	26.5	33.8
2	10	65	10	15	0	5.2	1.1	26.2	32.7
3	15	65	10	10	0	5.3	1.1	25.5	33.2
4	15	65	10	10	0	5.3	1.1	25.5	31.4
5	15	65	10	10	0	5.3	1.1	25.5	29.3
6	15	65	10	10	0	5.3	1.1	25.5	27.1
7	30	50	10	10	0	5.3	1.2	25.0	29.5
8	30	50	10	10	0	5.3	1.2	25.0	35.9
9	30	50	10	0	10	5.7	1.2	25.4	31.4
10	0	60	20	20	0	5.2	1.0	28.5	31.5
11	0	60	0	20	20	5.7	1.0	28.7	30.6
12	0	60	0	20	20	5.7	1.0	28.7	30.8
13	15	55	20	10	0	5.3	1.1	26.9	29.4
14	15	55	20	10	0	5.3	1.1	26.9	29.2
15	15	55	20	10	0	5.3	1.1	26.9	29.6
16	15	55	20	10	0	5.3	1.1	26.9	32.1
17	30	50	10	10	0	5.3	1.2	25.0	29.5
18	30	50	10	0	10	5.7	1.2	25.4	31.4

Results and Discussion

Coal Properties Selection: Linear Regression

Table 1 is presented the CRI and its corresponding coal properties. The lowest CRI was 16% which belonged to Coal-4 and Coal-11 categorized as hard-coking coal. The highest CRI was 46.2% shown by Coal-18 which was the semi-soft coking coal. Generally, the hard-coking coals has a low CRI. In contrast, the soft-coking coal has a high CRI. One may find a correlation by using linear regression to see how strong the relation between CRI and each coal properties.

There were nine variables of coal properties which suspected affecting the CRI was assessed by using linear regression. Those variables are Fe_2O_3, volatile matter (VM), reflectance vitrinite oil ($R_{v,max}$), SiO_2, TiO_2, K_2O, CaO, Na_2O, and Al_2O_3 percentage content in dry ash. A simple linear regression method was performed to observe the effect of each coal properties to the CRI. The linear regression equation is presented in the supporting information (Figure S1-S9). As seen in Figure S1-S9, the linear model failed to predict the CRI as indicated by the high standard error and low R^2 (<50%) of all coal properties presented in Table 3. In fact, four equations that correlated K_2O, CaO, Na_2O, dan Al_2O_3 percentage of dry ash coal with CRI showed very low R^2 (less than 10%). Hence, those four properties were eliminated from further consideration on the developed CRI prediction model. From initial screening, at least five most influencing coal properties to the CRI, i.e. Fe_2O_3, VM, $R_{v,max}$, SiO_2 dan TiO_2 were considered into the next stage of the coal properties selection process. The R^2 of those five properties equations were between 0.1 and 0.5.

Coal Properties Selection: Catalytic Effects

Further selection on the most important coal properties variable was conducted by considering the catalytic effect on the coke gasification process. The top three coal properties on the list that most affecting the CRI, i.e. Fe_2O_3 content in dry ash, VM, $R_{v,max}$, could be explained from the catalytic perspective of the coke gasification with carbon dioxide. Iron oxide content in its parent coal may act as a catalyst in the coke gasification process. The iron oxide could also more active as a catalyst after reduction process with the carbon monoxide resulted from coke gasification process as follows.

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)} \tag{9}$$

$$Fe_2O_{3(s)} + 3CO \rightarrow 2Fe + 3CO_{2(g)} \tag{10}$$

Monterroso et.al. reported that the iron-based catalyst was effectively improved the conversion rate of gasification low-sulfur sub-bituminous Wyodak coal (Monterroso et al. 2014). Thus, theoretically, the CRI is higher when using a high content of iron in the coals. CRI value was increase along with the Fe_2O_3 content which was in agreement

Table 3. R-squared and standard error of CRI estimated by linear regression.

No.	Parameters	R^2	Standard Error
1	Fe_2O_3	0.4841	6.9
2	VM	0.4190	7.4
3	Rv,max	0.3758	7.6
4	SiO_2	0.2776	8.2
5	TiO_2	0.1879	8.7
6	K_2O	0.0520	9.4
7	CaO	0.0437	9.5
8	Na_2O	0.0371	9.5
9	Al_2O_3	0.0001	9.7

with literature (Longbottom et al. 2016). Based on data in Table 1, the Fe_2O_3 content is relatively small within the range of 2% to 12% in the coal dry basis. Yet, the Fe_2O_3 content highly affected the CRI which suggested that the iron oxide content plays a role as a catalyst in the gasification reaction. Iron lowering the activation energy to make the gasification reaction faster. Hence, the CRI was increase as the iron oxide content increase.

The effect of volatile matter to the CRI clearly shown in Table 1. The higher volatile matter, the higher CRI value was observed. High volatile matter in coal might leave a large porosity and total surface area after carbonization in coke oven batteries. The high surface area and pore volume were reported to increase activity of alkane isomerization in silica alumina catalyst based (Kurniawan et al. 2018) and alkane cracking (Nasser et al. 2016). Typically, volatile matter in coke is very low which was reported less than 0.75% (Bertling 1999). Coke produced from a high-volatile matter coal was reported has a large porosity and surface area (Guo et al. 2016). The surface area has a strong effect on the oxidation reaction (Zamalloa and Utigard 1995). Hence, it is possible that the same condition occurs in the gasification process. The high surface area improves the mass transfer of carbon dioxide to react with carbon inside the pore. As the result, the conversion of coke into carbon monoxide increased.

Coal rank measured as reflectance vitrinite oil ($R_{v,max}$) shows that the higher coal rank the more difficult the produced coke to react with carbon dioxide. Coal rank shows the degree of coal age. The high number of coals rank the longer age of coal buried in the earth. The high coal rank most likely increases energy activation of gasification reaction on the CRI test. Hence, the gasification process will be slower when using a high coal rank.

The silica and titania content are considered to have no significant effect on the CRI. Silica is generally used as support material for catalyst actives metal. Hence, silica generally does not play an important role in catalytic process. Titania is a catalyst for reactions such as photocatalysis. However, the reaction of coke with carbon dioxide shows that the titania content is negatively weakly correlated with CRI (Fig. 4). The effect of coal rank clearly seen on those coal comparisons (Fig. 4). Based on these considerations, only three

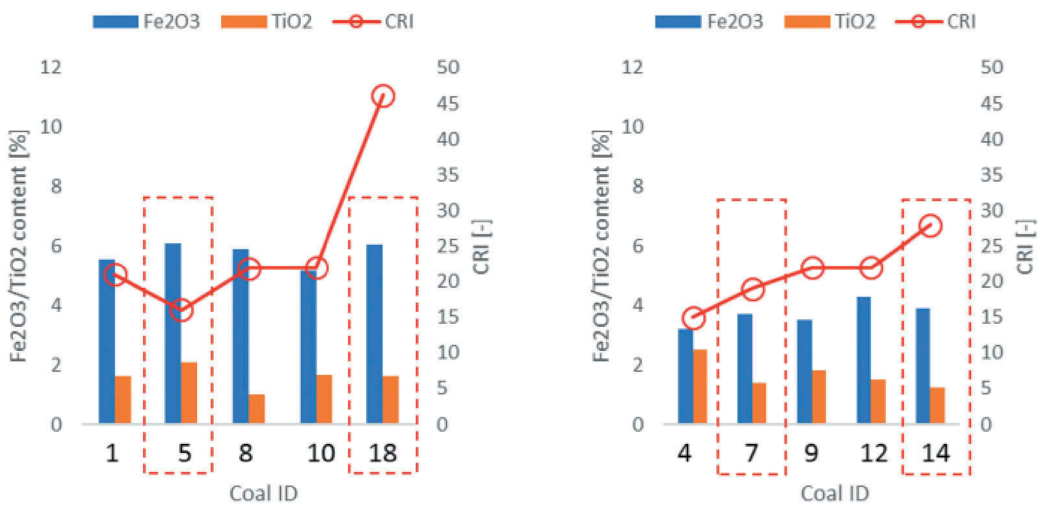


Figure 4. Comparison of the effect of Fe_2O_3 and TiO_2 content to CRI.

variables were taken into account in the CRI prediction model, i.e. the percentage of Fe_2O_3 in dry ash, volatile matter (VM), and $R_{v,max}$.

Kinetic Parameters Optimization

The volatile matter is most likely related to the surface area of coke (Sa) produced. The iron oxide content and coal rank ($R_{v,max}$) are most likely related to the activation energy (Ea) in the Arrhenius equation. Equation 4 is an ordinary differential equation containing kinetic parameters that must be optimized numerically using the least square method. The parameter estimated, A and Ea, was used to predict the CRI with Equation 1.

Therefore, we use those coal properties in the kinetic equation to predict CRI. Table 4 shows activation energy and rate constant after the optimization of CRI data with the kinetic model. Coal-18 shows the highest CRI of data and estimated CRI. Despite the activation energy was not the lowest, the rate constant is the highest among other coal because the contribution of volatile matter to create the surface area for the reaction is significant. Coal-4 shows the lowest CRI value of 15, while coal-6 shows the lowest value of CRI prediction.

CRI and CSR Prediction of Single Coal

Figure 5 shows that the CRI prediction is in a good agreement with the CRI data with R^2 = 0.84 and standard error = 4.5%. Coal 4 shows the same CRI prediction results as the CRI obtained from the laboratory. Coal-4 hard coking coal produces the highest quality coke compared to other coal, based on the CRI. Coal-18 coal produced coke with the highest predicted CRI of 48.8% which was slightly different from the CRI data, which was 46.2%.

CSR has a strong linear correlation with CRI as shown in Fig. 6 with R^2 = 0.88. This is in a good agreement with literature which reported a high R^2 of correlation between CSR and CRI within the range of 0.79–0.98 (Karunova, Gyul'maliev, and Gagarin 2009;

Table 4. Kinetic parameters of individual coal for CRI prediction.

No	Coal ID	Ea (J/mol)	$k' \times 10^5$ (1/s)	CRI [%]	CRI prediction [%]
1	Coal-1	444055	2.78	21	18.0
2	Coal-2	442963	2.57	24	16.8
3	Coal-3	441113	3.72	27	23.4
4	Coal-4	446666	2.29	15	15.0
5	Coal-5	443491	3.09	16	19.8
6	Coal-6	447637	2.16	22	14.2
7	Coal-7	446111	2.36	19	15.4
8	Coal-8	441702	4.02	21.9	25.0
9	Coal-9	445555	2.80	22	18.1
10	Coal-10	443225	3.45	22	21.8
11	Coal-11	446747	2.59	15	16.8
12	Coal-12	444582	2.96	22	19.0
13	Coal-13	445005	3.10	28	19.9
14	Coal-14	439828	5.78	26.4	33.9
15	Coal-15	443299	4.04	24	25.1
16	Coal-16	436030	7.64	39	42.2
17	Coal-17	434388	8.60	44.5	46.1
18	Coal-18	437443	9.33	46.2	48.8
19	Coal-19	440865	6.33	31.7	36.5
20	Coal-20	436672	6.41	41	36.8

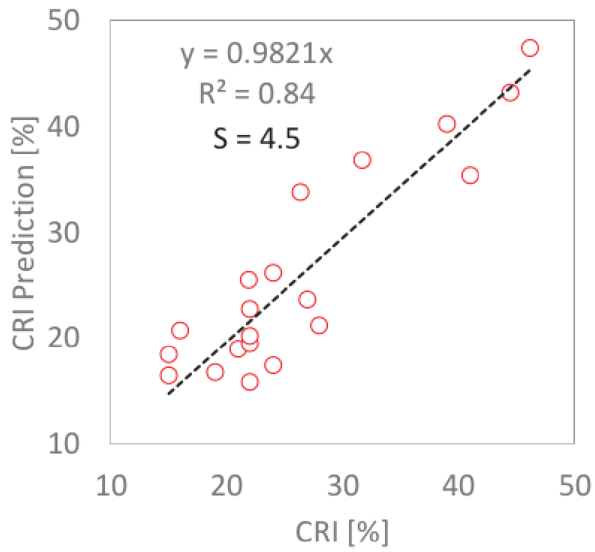


Figure 5. CRI prediction vs CRI data.

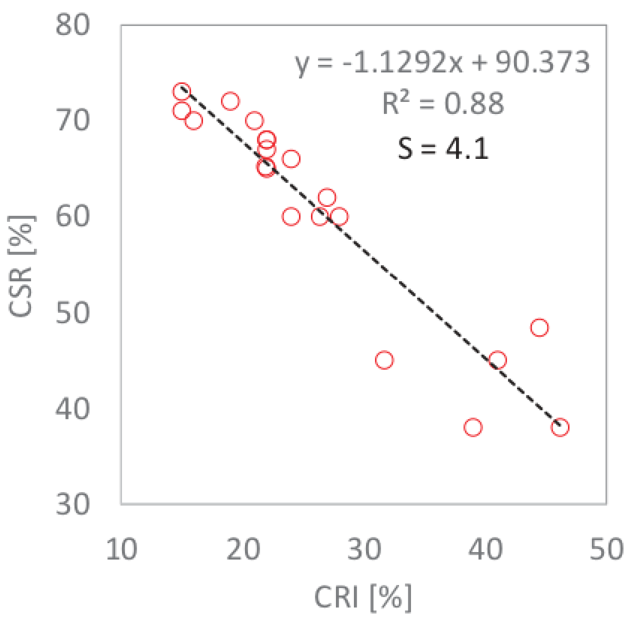


Figure 6. Correlation of CRI and CSR.

Lyalyuk et al. 2010; Nag et al. 2009; Rodero et al. 2015). Hence, we can use the correlation to predict the CSR from the estimated CRI by using Equation 11. The results of predicted CSR are compared with CSR data shown in Fig. 7 and Table 5. One can see that the CSR predicted is in a good agreement with CSR data with R^2 = 0.86.

$$CSR = -1.1292CRI + 90.373 \tag{11}$$

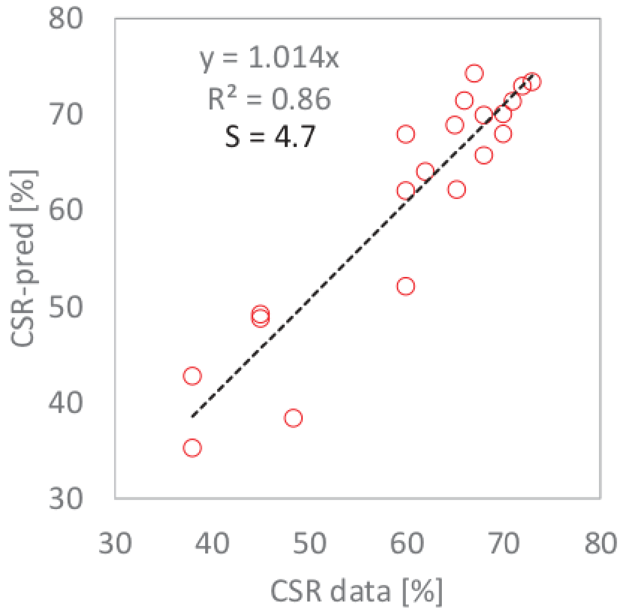


Figure 7. CSR prediction vs CSR data.

Table 5. CSR prediction by using linear regression equation.

No	Coal ID	CSR [%]	CSR prediction [%]
1	Coal-1	70	70.1
2	Coal-2	66	71.5
3	Coal-3	62	64.0
4	Coal-4	73	73.4
5	Coal-5	70	68.0
6	Coal-6	67	74.3
7	Coal-7	72	72.9
8	Coal-8	65.2	62.2
9	Coal-9	68	69.9
10	Coal-10	68	65.7
11	Coal-11	71	71.4
12	Coal-12	65	68.9
13	Coal-13	60	68.0
14	Coal-14	60	52.1
15	Coal-15	60	62.0
16	Coal-16	38	42.7
17	Coal-17	48.4	38.4
18	Coal-18	38	35.2
19	Coal-19	45	49.2
20	Coal-20	45	48.8

The maximum CSR of laboratory data is indicated by coke originating from Coal-4 coal with CSR = 73% which is very close to the predicted CSR of 73.4%. The minimum CSR from laboratory data is shown by coke produced from coal Coal-18 with CSR = 38% and CSR prediction results showing 35.2%. Overall, the error between CSR predictions and actual CSR is less than 5%. High-quality coke indicated with a high CSR and low CRI. Based on the model developed, high-quality coke could be obtained from coal with low VM content, high coal rank ($R_{v,max}$), and low Fe_2O_3 content.

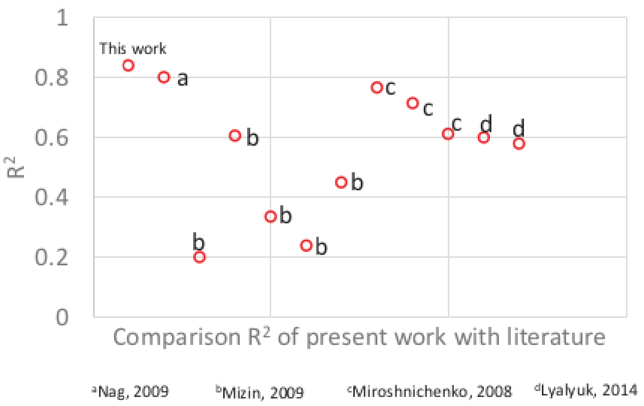


Figure 8. Comparison of CRI prediction accuracy of the developed kinetic model with literature.

The comparison of present work with literature is presented in Fig. 8 (Lyalyuk et al. 2014; Miroshnichenko 2008; Mizin, Zinov'eva, and Klyukin 2009; Nag et al. 2009). The data comparison suggested that the developed kinetic model for CRI prediction is more accurate as compared with statistical regression or other methods reported in literature. Furthermore, the developed kinetic model give a physical explanation of how coal properties affecting the CRI through coke catalytic gasification reaction.

Sensitivity Analysis of Fe_2O_3, Coal Rank, and Volatile Matter on the CRI

One can easily see how the iron oxide content in coal affected the coke reactivity through kinetic model as presented in Fig. 9a,b. As the iron oxide content increase, the coke converted into carbon monoxide was increase. Iron oxide acted as a catalyst providing active sites for reaction in the gasification coke test. As a result, the CRI is getting higher when Fe_2O_3 in coal is high. This is in agreement with literature which suggested that iron oxide on silica alumina support showed catalytic activity for tar cracking (Adnan et al. 2017). The authors suggested that the high content of iron oxide led to a high number of strong acid sites according to ammonia TPD data which responsible for the high activity of cracking tar.

The effect of the iron content in coal on CRI was studied further using the developed kinetic model. The value of $R_{v,\ max}$ and VM were set to a constant, i.e. 1.2% and 24.6%, respectively. On the other hand, the percentage of Fe_2O_3 in dry ash was varied from 2% to 12%. The selection of iron percentage ranges is based on the minimum and maximum iron content in coal ash taken from laboratory data. In the CRI test, 200 g of coke was reacted with carbon dioxide at a temperature of 1100°C for 2 h. Coke derived from coal with the lowest Fe_2O_3 content shows the slowest reaction as seen in Fig. 9a. Accordingly, the amount of coke from coal with the highest content of Fe_2O_3 was decrease faster among others. The high iron content in coal makes the gasification reaction rate increase significantly. The CRI is determined based on the percentage of weight loss of coke. Based on Equation 1, the percentage range of coal can be predicted to obtain coke with the desired CRI. Most of industry required coke with CRI less than 20–30% (Rodero et al.

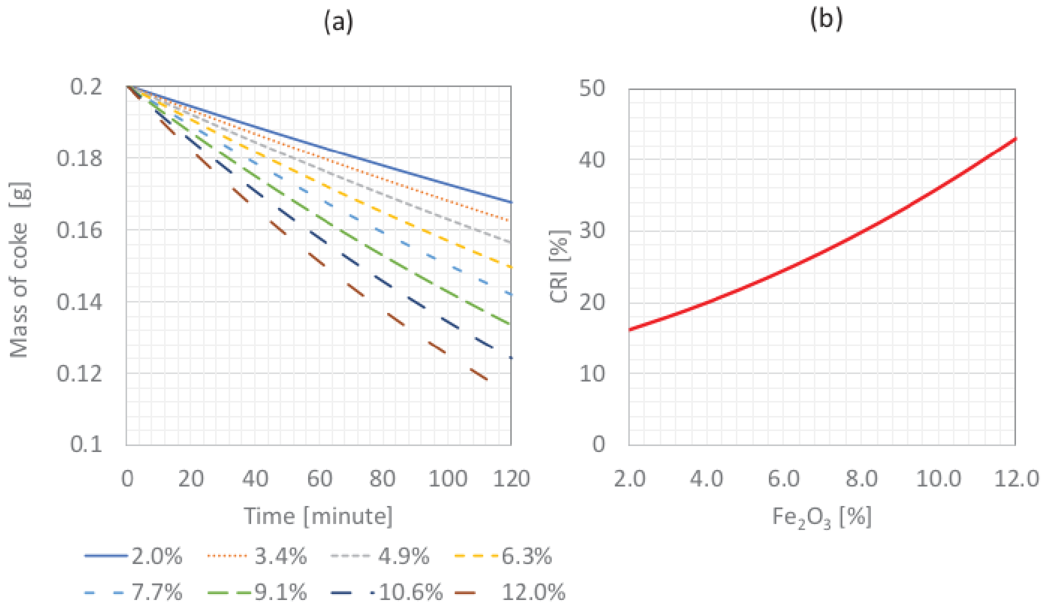


Figure 9. Catalytic effect of coal iron oxide content on CRI: (a) kinetic of coke gasification (b) CRI vs Fe_2O_3.

2015). For the sensitivity analysis purpose, the CRI less than 25% was the target of the simulation in our study.

The simulation showed that coal with 2% Fe_2O_3 resulted in CRI 16%. The coal with maximum iron oxide content of 12% gave CRI 42.5% which is beyond the CRI target. Coal with iron oxide content up to 6.1% is predicted to provide a CRI of less than 25%. Coal with an iron content of more than 6.1% will produce coke with a CRI greater than 25% (Fig. 9b). Hence, the recommended range of content of Fe_2O_3 in coal dry ash is less than 6.1% to obtain CRI less than 25%. The range of iron content can be wider by choosing coal that has a lower VM and higher coal rank.

Sensitivity analysis of the effect of $R_{v,max}$ coal on reducing coke mass in the CRI test reactor is presented in Fig. 10a. The percentage of Fe_2O_3 and VM is considered constant, which is 5.75% and 24.6%, respectively. $R_{v,max}$ was varied from 0.8% to 1.6%. The selection of the range of $R_{v,max}$ is based on the minimum and maximum content of coal rank taken from the data laboratory. Coke originating from coal with the lowest $R_{v,max}$, converted into gas faster among others as seen in Fig. 10a. On the other hand, coke derived from coal with the highest $R_{v,max}$ reacted slower. The high degree of coal rank makes the gasification reaction rate decrease.

The result of CRI calculation showed that coal with $R_{v,max}$ 0.8% resulted in CRI 32% and coal with $R_{v,max}$ 1.6% led to CRI 20.5%. Coal with $R_{v,max}$ greater than 1.15% is predicted to provide CRI of less than 25%. On the other hand, coal with $R_{v,max}$ less than 1.15% estimated to produce coke with CRI greater than 25% (Fig. 10b). The value of Fe_2O_3 and VM were set to a constant which are 5.75% and 24.6%, respectively. The percentage $R_{v,max}$ is must less than 1.15% to obtain coke with CRI<25%. The percentage $R_{v,max}$ range can be widened by choosing coal that has lower Fe_2O_3 and VM content.

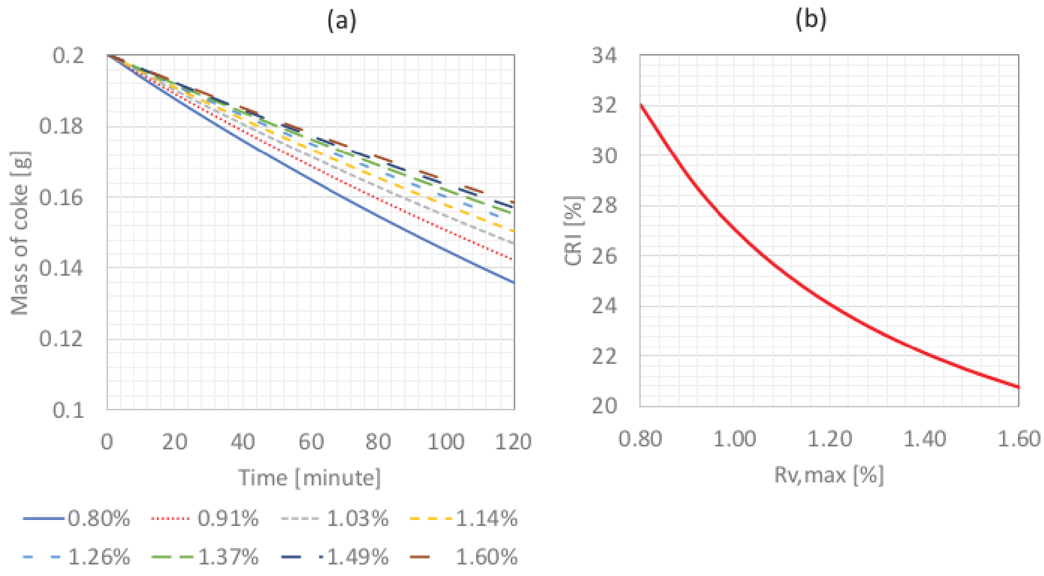


Figure 10. Catalytic effect of coal rank on CRI coke: (a) kinectic of coke gasification (b) CRI vs $R_{v,max}$.

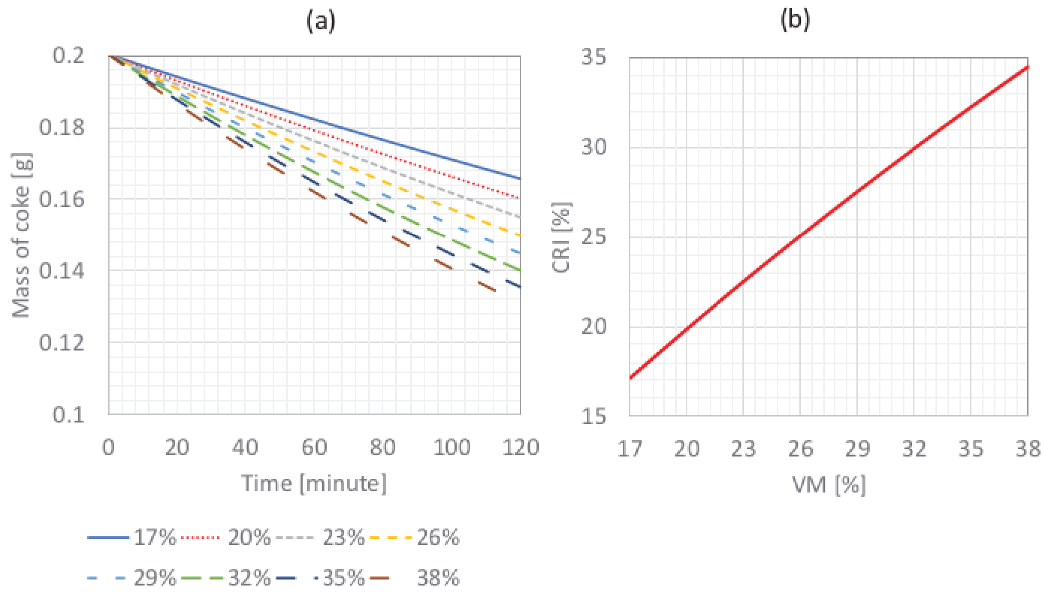


Figure 11. Catalytic effect coal volatile matter on CRI coke: (a) kinetic of coke gasification (b) CRI vs VM.

The catalytic effect of volatile matter on CRI is shown in Fig. 11a,b. The value of Fe_2O_3 and $R_{v,max}$ were set constants, which were 5.75% and 1.2%, respectively. The VM content is varied from 17% to 38% which is the minimum and maximum content of coal taken from the data. Coke derived from coal with the lowest VM reacted slower among others (Fig. 11a). In contrast, coke derived from coal with the highest VM content reacted faster.

Table 6. CRI of coal blending data and estimated.

Blending No.	Coal-1 [%]	Coal-10 [%]	Coal-18 [%]	Coal-19 [%]	Coal-21 [%]	CRI [%]	CRI Prediction [%]
1	15	60	25	0	0	33.8	31.3
2	10	65	10	15	0	32.7	30.0
3	15	65	10	10	0	33.2	28.9
4	15	65	10	10	0	31.4	28.9
5	15	65	10	10	0	29.3	28.9
6	15	65	10	10	0	27.1	28.9
7	30	50	10	10	0	29.5	28.0
8	30	50	10	10	0	35.9	28.0
9	30	50	10	0	10	31.4	30.0
10	0	60	20	20	0	31.5	34.3
11	0	60	0	20	20	30.6	37.1
12	0	60	0	20	20	30.8	37.1
13	15	55	20	10	0	29.4	31.5
14	15	55	20	10	0	29.2	31.5
15	15	55	20	10	0	29.6	31.5
16	15	55	20	10	0	32.1	31.5
17	30	50	10	10	0	29.5	28.0
18	30	50	10	0	10	31.4	30.0

The high content of VM makes the gasification reaction faster because of the increase of mass transfer rate as the result of high porosity formed during carbonization in the coke oven batteries.

The CRI calculation results showed that coal with a 17% VM gives a CRI of 17%. Accordingly, coal with a 38% VM gives a CRI of 35%. Coal with VM of less than 26% is predicted to provide a CRI of less than 25%. Coal with a VM of more than 26% is estimated to produce coke with a CRI greater than 25% (Fig. 11b). The percentage range of VM content can be extended by selecting coal which has lower Fe_2O_3 content and higher $R_{v,max}$.

According to the sensitivity analysis of coal properties, iron oxide percentage was the most significant coal properties that affected CRI as compared with VM and coal rank. This is most likely because the content of Fe_2O_3 acts as a catalyst which decreases activation energy. It is worth to mention that the activation energy parameter is in the exponential term of the Arrhenius equation. Hence, a small change in the number of activation energy lead to a significant difference in the rate of coke gasification reaction rate.

CRI of Coal Blending

The coal blends were from the hard-coking coal (Coal-1 and Coal-10) and semi-soft coking coal (Coal-18, Coal-19, Coal-21) as presented in Table 6. Figure 12 shows that the CRI predicted is in agreement with the CRI data. The calculated standard error was relatively low ca. 3.7 even lower as compared with the single coal with ca. 4.7. The kinetic model was also applied using coal blends data from literature (Lyalyuk et al. 2014). Figure 13 shows that the present model has the lowest standard error, ca. 1.3, among other methods which indicated that the kinetic model was appropriate to apply for CRI prediction. From our data calculation and data literature, the kinetic approach was proven to be able to predict the CRI from its coal blends properties.

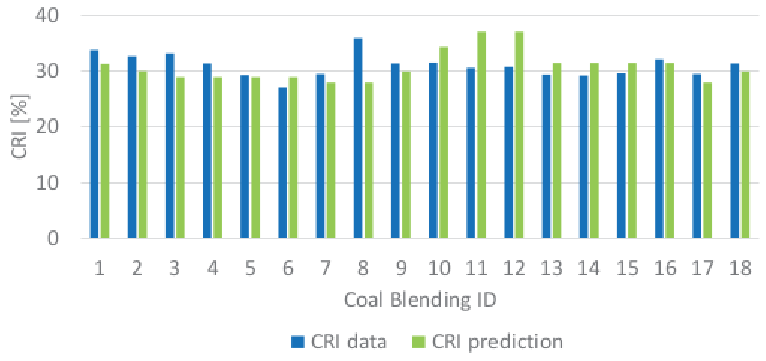


Figure 12. CRI data vs CRI prediction of coke from its coal blend properties.

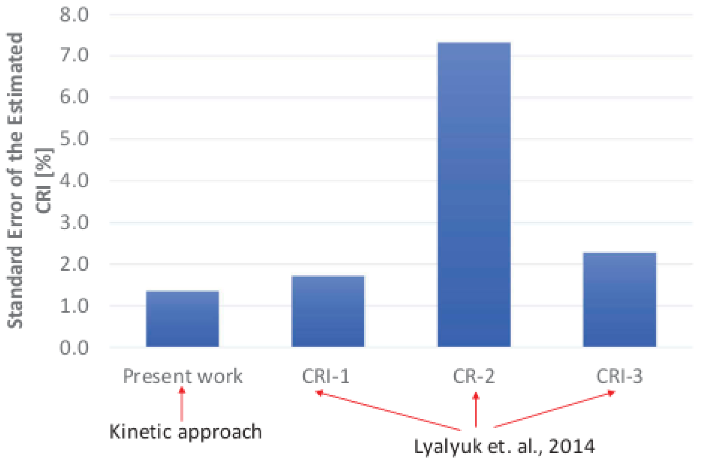


Figure 13. Standard error of estimated CRI by kinetic model for coal blend using data from literature.

Conclusion

The CRI prediction model has been developed based on mass balance and kinetic model of batch reactor of CRI test. Three main properties of coals, i.e., Fe_2O_3 content, volatile matter, and coal rank were selected to predict the CRI. Kinetic parameters of the model were resolved using the non-linear least squared method. The CSR model has been developed by linear regression between CSR and CRI data. The predicted CRI value was in a good agreement with the CRI data (R^2 = 0.84). The estimated CSR value was in a good agreement with the CSR data (R^2 = 0.86). The sensitivity analysis of the effect of iron oxide, volatile matter, and coal rank was also performed using the developed kinetic model. Finally, the model was successfully applied for coal blending to estimate CRI of the produced coke from its coal blend properties.

References

Adnan, M. A., O. Muraza, S. A. Razzak, M. M. Hossain, and H. I. de Lasa. 2017. Iron oxide over silica-doped alumina catalyst for catalytic steam reforming of toluene as a surrogate tar biomass species. *Energy & Fuels* 31:7471–81. doi:10.1021/acs.energyfuels.7b01301.

Bertling, H. 1999. Coal and coke for blast furnaces. *ISIJ International* 39:617–24. doi:10.2355/isijinternational.39.617.

Díaz-Faes, E., C. Barriocanal, M. A. Díez, and R. Alvarez. 2007. Applying TGA parameters in coke quality prediction models. *Journal of Analytical and Applied Pyrolysis* 79:154–60. doi:10.1016/j.jaap.2006.11.001.

Flores, B. D., I. V. Flores, A. Guerrero, D. R. Orellana, J. G. Pohlmann, M. A. Diez, A. G. Borrego, E. Osório, and A. C. F. Vilela. 2017. Effect of charcoal blending with a vitrinite rich coking coal on coke reactivity. *Fuel Processing Technology* 155:97–105. doi:10.1016/j.fuproc.2016.04.012.

Guo, R., W.-J. Hu, Y.-H. Liang, and Q. Wang. 2016. Effects of coking coal properties on coke pore structure: Prediction models. *Metallurgical Research & Technology* 113:404. doi:10.1051/metal/2016018.

Gyul'maliev, A. M., S. G. Gagarin, Y. V. Konovalova, and I. A. Sultanguzin. 2002. Estimation of the reactivity and strength of coke based on the kinetic of its interaction with carbon dioxide. *Solid Fuel Chemistry* 36:33–42.

Karunova, E. V., A. M. Gyul'maliev, and S. G. Gagarin. 2009. Use of the petrographic model for coke quality prediction at the cherepovets iron-and-steel mill. *Solid Fuel Chemistry* 43:351. doi:10.3103/S0361521909060032.

Kurniawan, T., O. Muraza, I. A. Bakare, M. A. Sanhoob, and A. M. Al-Amer. 2018. Isomerization of n-butane over cost-effective mordenite catalysts fabricated via recrystallization of natural zeolites. *Industrial & Engineering Chemistry Research* 57:1894–902. doi:10.1021/acs.iecr.7b04040.

Li, K., R. Khanna, J. Zhang, Z. Liu, V. Sahajwalla, T. Yang, and D. Kong. 2014. The evolution of structural order, microstructure and mineral matter of metallurgical coke in a blast furnace: A review. *Fuel* 133:194–215. doi:10.1016/j.fuel.2014.05.014.

Longbottom, R. J., B. J. Monaghan, A. A. Chowdhury, M. H. Reid, G. Zhang, M. R. Mahoney, and K. Hockings. 2016. Effect of mineral matter on the reactivity of coke and its replication in a coke analogue. *ISIJ International* 56:1553–58. doi:10.2355/isijinternational.ISIJINT-2015-597.

Lyalyuk, V. P., V. A. Sheremet, A. V. Kekuh, P. I. Otorvin, A. K. Tarakanov, and D. A. Kassim. 2010. Investigation of coke reactivity effect on parameters of blast furnace operation. *Metallurgical and Mining Industry* 2:317–23.

Lyalyuk, V. P., V. P. Sokolova, E. O. Shmeltser, D. Y. Timofeeva, and V. V. Beryeza. 2014. Predicting the reactivity and hot strength of coke on the basis of ash basicity. *Coke and Chemistry* 57:238–44. doi:10.3103/S1068364X14060052.

MacPhee, T., L. Giroux, K. W. Ng, T. Todoschuk, M. Conejeros, and C. Kolijn. 2013. Small scale determination of metallurgical coke CSR. *Fuel* 114:229–34. doi:10.1016/j.fuel.2012.08.036.

Miroshnichenko, D. V. 2008. Preliminary estimation of coke's CRI and CSR values on the basis of the physical properties of coal ash. *Coke and Chemistry* 51:447–50. doi:10.3103/S1068364X08110057.

Mizin, V. G., L. A. Zinov'eva, and S. N. Klyukin. 2009. Assessing the metallurgical coke produced at OAO NLMK. *Coke and Chemistry* 52:412–17. doi:10.3103/S1068364X09090087.

Monterroso, R., M. Fan, F. Zhang, Y. Gao, T. Popa, M. D. Argyle, B. Towler, and Q. Sun. 2014. Effects of an environmentally-friendly, inexpensive composite iron–sodium catalyst on coal gasification. *Fuel* 116:341–49. doi:10.1016/j.fuel.2013.08.003.

Nag, D., S. K. Haldar, P. K. Choudhary, and P. K. Banerjee. 2009. Prediction of coke CSR from ash chemistry of coal blend. *International Journal of Coal Preparation and Utilization* 29:243–50. doi:10.1080/19392690903218117.

Nasser, G. A., T. Kurniawan, T. Tago, I. A. Bakare, T. Taniguchi, Y. Nakasaka, T. Masuda, and O. Muraza. 2016. Cracking of n-hexane over hierarchical MOR zeolites derived from natural minerals. *Journal of the Taiwan Institute of Chemical Engineers* 61:20–25. doi:10.1016/j.jtice.2015.11.025.

North, L., K. Blackmore, K. Nesbitt, and M. R. Mahoney. 2018. Models of coke quality prediction and the relationships to input variables: A review. *Fuel* 219:446–66. doi:10.1016/j.fuel.2018.01.062.

Pusz, S., and R. Buszko. 2012. Reflectance parameters of cokes in relation to their reactivity index (CRI) and the strength after reaction (CSR), from coals of the Upper Silesian Coal Basin, Poland. *International Journal of Coal Geology* 90–91:43–49. doi:10.1016/j.coal.2011.10.008.

Rodero, J. I., J. Sancho-Gorostiaga, M. Ordiales, D. Fernández-González, J. Mochón, I. Ruiz-Bustinza, A. Fuentes, and L. F. Verdeja. 2015. Blast furnace and metallurgical coke's reactivity and its determination by thermal gravimetric analysis. *Ironmaking & Steelmaking* 42:618–25. doi:10.1179/1743281215Y.0000000016.

Song, T., J. Zhang, G. Wang, H. Wang, R. Xu, Q. Pang, and C. Wang. 2018. Effect of carbonization conditions on the property and structure of bamboo char for injection in blast furnace. *ISIJ International* 59:442–449.

Stanford, C. E. 2013. 9 - Coal resources, production and use in Indonesia. In *The coal handbook: Towards cleaner production*, ed. D. Osborne, 200–19. Cambridge, UK: Woodhead Publishing.

Tiwari, H. P., P. K. Banerjee, and V. K. Saxena. 2013. A novel technique for assessing the coking potential of coals/coal blends for non-recovery coke making process. *Fuel* 107:615–22. doi:10.1016/j.fuel.2012.12.015.

Ulanovskiy, M. L. 2014. Ash basicity and the coke characteristics CRI and CSR: A review. *Coke and Chemistry* 57:91–97. doi:10.3103/S1068364X14030089.

Wang, Q., R. Guo, X.-F. Zhao, J.-F. Sun, S. Zhang, and W.-Z. Liu. 2016. A new testing and evaluating method of cokes with greatly varied CRI and CSR. *Fuel* 182:879–85. doi:10.1016/j.fuel.2016.05.101.

Yang, Y., K. Raipala, and L. Holappa. 2014. Chapter 1.1 - Ironmaking. In *Treatise on process metallurgy*, ed. S. Seetharaman, 2–88. Boston: Elsevier.

Yustanti, E. 2012. Pencampuran Batubara Coking Dengan Batubara Lignite Hasil Karbonisasi Sebagai Bahan Pembuatan Kokas. *Jurnal Teknologi Pengelolaan Limbah* 15:15–30.

Zamalloa, M., and T. A. Utigard. 1995. Characterization of industrial coke structures. *ISIJ International* 35:449–57. doi:10.2355/isijinternational.35.449.

Kinetik Model 2020

ORIGINALITY REPORT

8%	8%	3%	3%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	tandf.figshare.com Internet Source	4%
2	Submitted to School of Business and Management ITB Student Paper	1%
3	files.eric.ed.gov Internet Source	1%
4	Muflih A. Adnan, Oki Muraza, Shaikh A. Razzak, Mohammad M. Hossain, Hugo I. de Lasa. "Iron Oxide over Silica-Doped Alumina Catalyst for Catalytic Steam Reforming of Toluene as a Surrogate Tar Biomass Species", Energy & Fuels, 2017 Publication	1%
5	vdocuments.site Internet Source	1%

Exclude quotes	On	Exclude matches	< 1%
Exclude bibliography	On		