

Effects of an environmentally-friendly, inexpensive composite iron–sodium catalyst on coal gasification



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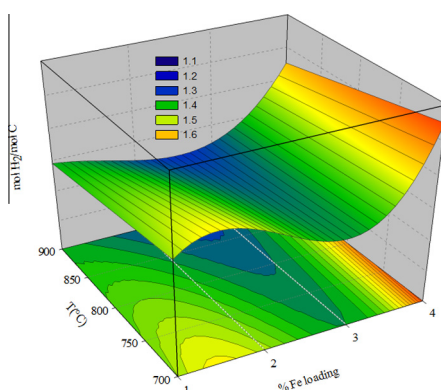
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HIGHLIGHTS

- The effects of a composite catalyst on coal gasification were evaluated.
- The use of the composite can improve the yields of useful gases.
- The composite catalyst can combine the advantages of its two component catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of this research is to study the effect of the composite catalyst, $\text{FeCO}_3\text{--Na}_2\text{CO}_3$, on gasification of a low-sulfur sub-bituminous Wyodak coal from the Powder River Basin (PRB) of Wyoming. The catalytic effects of the composite catalysts were evaluated by comparing their effluent gas compositions and carbon conversion kinetics to those achieved in the presence of either FeCO_3 or Na_2CO_3 catalyst alone or without the presence of any catalyst. All of the evaluation work was conducted in a fixed bed gasifier at atmospheric pressure. Compared to raw coal with no catalyst, the composite catalyst is efficient in increasing the carbon conversion rate constant by as much as two times within the 700–800 °C range due to its ability to reduce the activation energy of gasification by about 30–40%. Compared to pure sodium and iron catalysts, the composite catalyst can increase the yields of desired products H_2 and CO at 800 °C by 15% and 40%, respectively. The composite catalyst can not only synergize the advantages, but also overcome the challenges of pure iron or pure sodium based catalytic coal gasification processes.

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1. Introduction

Coal gasification has been commercially used for over 60 years in the production of fuels and chemicals [1]. Due to the reduced environmental impacts and the high efficiency obtained from

integrated gasification combined cycle (IGCC) processes, coal gasification has recently received increased attention. Since the energy needed to achieve gasification temperatures is obtained from exothermic combustion reactions prior to gasification, the rate at which the pre-gasification step and gasification occur need to be increased in order to achieve lower operating temperatures to consume less energy. Furthermore, there is a need to increase the ratio of gases that preserve the highest heat of combustion, e.g., carbon

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monoxide (CO) and hydrogen (H₂) vs. carbon dioxide (CO₂) and water (H₂O). Catalysts have the potential to achieve both of these desired effects.

Catalytic coal gasification is one of the main techniques used to improve the gasification process due to its efficiency, availability, and low cost [1–4]. Moreover, catalysts have the capacity of lowering the gasification temperature, increasing conversion rates, and enhancing the production of the desired gases by changing the selectivity in the process [4,5]. As a result, the life span of the gasifiers can be increased, especially when the chosen catalyst is non-corrosive. Different catalysts have been studied in the past demonstrating such results [1–8]. Catalytic coal gasification has shown substantial decreases in the activation energy associated with the process [1,2,7,9]. Otto and Shelef showed that, in many cases, this reduction results from improved mass transport or diffusion affected by the porosity of the catalytically gasified carbons [9]. A few previously studied coal gasification catalysts are K₂CO₃, Li₂CO₃, Na₂CO₃, Ca(OH)₂ and their combinations, for example, Wang et al. studied the synergistic effect of using Ca(OH)₂ in char preparation for K₂CO₃ catalyzed coal gasification [7,10]. After pyrolysis, the retention of many of these salts in the char diminishes adverse impacts on the gasification operation and enhances the conversion of the solid char [8]. For example, Douchanov and Angelova [7] studied the effect of 13 metallic salts on the gasification rate of a lignite coal and found considerable improvements when comparing these rates to those obtained with non-catalytic coal gasification. Kasaoka et al. [11] also studied the effect of Fe, Co, Ni, Zn, and Li on different types of activated carbon and other coal chars using non-coking coal from Uonuki in Japan, moderate coking coal from Kuznetsk in Russia, and strong coking Pittston coal from Pennsylvania. Their interests were concentrated on the properties of the non-carbonate ferrous catalyst and on the role played by the inlet gas or mixture of gases [11].

Iron based catalysts have demonstrated many benefits, such as low price, availability, and environmental friendliness [1–4,6]. Different iron compounds have been tested as catalysts for coal gasification with encouraging results. Recently, FeCO₃ was found to be a promising catalyst for considerable reduction of the activation energy of the gasification of a subbituminous Wyodak coal [3]. Additionally, the iron based catalyst demonstrated its strong ability in significantly alleviating the tar issue often met in gasification, as reported by Popa et al., Nordgreen et al., [3,12–14]. Cypres and Soudan-Moinet, determined that while ferric oxide and ferrous oxide did not possess any catalytic activity, the tars were initially oxidized, the devolatilization rate during pyrolysis of the coal was reduced, and the composition of the tar remained unchanged [14]. These researchers observed that hematite, produced by the addition of iron as a catalyst, has a high impact on tar breakdown [14]. They also observed that the extent of this effect is larger with hematite (Fe₂O₃) than with magnetite (Fe₃O₄) or wüstite (FeO) [14]. These findings were observed more prominently through the 600–800 °C temperature range [14].

Sodium based catalysts which are widely available and inexpensive also exhibit great potential in improving the kinetics of the gasification [1,2,4,6,15]. Popa et al. [2] found increases in the carbon conversion rates during both pyrolysis and gasification steps and a decrease in the activation energy when Na₂CO₃ was used as a catalyst. Conversely, one problem that has been encountered with the use of Na₂CO₃ is the formation of more non-volatile tars that condense at lower temperatures downstream of the gasifier [2]. Liquid tar from coal gasification produces a number of adverse effects throughout the process, including plugging. The removal of this material is complicated because it combines with sticky ash and turns into a highly viscous paste [1]. Thus, the overall efficiency of the process is hindered and less desirable in terms of cost-effectiveness and applicability.

In order to overcome the shortcomings of individual sodium or iron based catalysts, a few gasification studies have been performed using sodium and iron composite catalysts, and favorable results have been achieved [4,6,8,16]. However, the reported composite catalysts contain anions including NO₃[−] and SO₄^{2−}, which are potentially harmful to gasifier and undesired for production of high-quality syngas. Accordingly, this research was designed to evaluate the effect of new composite catalysts consisting of less corrosive and environmentally acceptable carbonates (FeCO₃ and Na₂CO₃) on coal gasification.

2. Experiments

2.1. Coal analysis

2.1.1. Thermo-gravimetric analysis

Thermo-gravimetric analyses (TGA) of the Wyodak low-sulfur sub-bituminous coal from the Powder River Basin (PRB) of Wyoming and catalyst samples were performed using a TA Instruments SDT Q600 apparatus. A 50 mg sample of coal and catalyst, loaded on a ceramic capped alumina sample holder, was heated at 20 °C/min in flowing Ar or N₂ (Ultra High Purity (UHP), US Welding) at 100 ml/min to a maximum pyrolysis temperature of 1,200 °C and held at this temperature for another 10 minutes for isothermal equilibration.

2.1.2. Ultimate and proximate analyses

The results of proximate and ultimate analyses of the coal used in this study are described elsewhere [2]. The proximate analyses were performed according to ASTM D5142 and D5016. The ultimate analyses were performed on PRB chars obtained at 700 °C, 800 °C and 900 °C by ASTM D5373, D5016, and D4239 methods.

2.2. Catalysts

2.2.1. Catalyst preparation

Aqueous solutions were prepared by mixing FeSO₄·7H₂O (99%, Sigma-Aldrich) with Na₂CO₃ (99.8 wt%, FMC Inc.) in a 10% (w/w) solution. The resulting FeCO₃ precipitate was filtered, washed with sodium carbonate and distilled water, dried at 92 °C, and calcined at 250 °C to form a brown powder. This material (FeCO₃) was screened on a 125 μm sieve to exclude larger particles and stored in air tight, dark colored containers in order to prevent structural and moisture content changes. Additionally, Na₂CO₃ 10% (w/w) solutions were prepared with Na₂CO₃ (99.8 wt%, FMC Inc.).

2.2.2. Catalyst loading on coal

In this study, pure FeCO₃, pure Na₂CO₃, and FeCO₃–Na₂CO₃ were loaded with coal for catalytic gasification. The catalyst and coal mixtures were prepared by adding the appropriate amounts of FeCO₃, Na₂CO₃ or FeCO₃–Na₂CO₃ to PRB pulverized (200 mesh) coal to obtain the following weight ratios of catalyst to dry ash free (DAF) basis coal: 0%-Fe + 4%-Na, 1%-Fe + 3%-Na, 2%-Fe + 2%-Na, 3%-Fe + 1%-Na, and 4%-Fe + 0%-Na. The pure iron catalyst and coal mixture was produced by loading the appropriate amount of FeCO₃ with coal to obtain the desired weight of iron in the mixture, then mixing it and subsequently adding water to create a paste which was dried at 90 °C for 72 h prior to gasification. The pure sodium catalyst and coal mixture and the composite catalyst and coal mixtures were prepared using the same procedure.

2.3. Catalytic gasification tests

The fixed-bed reactor used for pyrolysis and gasification experiments is described elsewhere [2]. Gaseous product compositions

were measured by gas chromatography [2]. The experiments were carried out using approximately 5.0 g DAF coal samples, which were initially pyrolyzed by heating at 20 °C/min to the desired gasification temperatures of 700 °C, 750 °C, 800 °C, 850 °C, and 900 °C in flowing N₂. The resulting chars were then gasified by introducing H₂O and N₂ with flow rates of 0.04 g/min and 4.1 ml/min, respectively. The gasification experiments were performed at ambient atmospheric pressure (approximately 75 kPa at the elevation of our laboratory).

3. Results and discussion

3.1. Effect of catalyst on pyrolysis

Fig. 1 shows the pyrolysis results of four Wyodak coals from Wyoming Powder River (PBR) loaded with different composite catalysts. The pyrolysis results of the coal with the 0%-Fe + 4%-Na catalyst was published elsewhere [2]. Fig. 1 shows that the 3%-Fe + 1%-Na catalyst was the most effective in increasing the rate of pyrolysis because it led to the highest mass loss during pyrolysis process. The coals loaded with 4%-Fe + 0%-Na and the 2%-Fe + 2%-Na catalysts displayed the lowest pyrolysis rates, with 2%-Fe + 2%-Na lagging initially at temperatures below ~375 °C, while 4%-Fe + 0%-Na had the least mass loss between about 500 and 750 °C. Despite these differences, all of the coal samples reached approximately the same mass at temperatures higher than ~750 °C. All the tests were performed three times at the same conditions. The reported data are the average values of these triplicate experiments.

3.2. Factors affecting yields of CO, CO₂ and H₂

The composition of the generated syngas is important since it is not only one of the indicators of the overall performance of the gasification process, but also affects the potential uses of the syngas. Methane (CH₄) was not studied in detail in this research because of low (<1% of the gaseous product) yields obtained in all experiments due to the coal used and the gasification conditions chosen for the research. Mass balances were performed to obtain the yields of CO and H₂ based on the remaining mass of char after pyrolysis up to the gasification test temperature and the amount of carbon in the char, which were obtained from the TGA and ultimate analyses, respectively. The ultimate analyses of the char samples generated from the coal loaded with various amounts of the composite catalysts at different temperatures are listed in Table 1. The carbon content generally increased at the expense of hydrogen

and oxygen with increasing pyrolysis temperatures, consistent with the formation of more refractory chars.

3.2.1. Composition of the catalysts and pyrolysis temperature

Fig. 2 shows the hydrogen molar yield (normalized per mole of carbon in the char) as a function of iron loading and pyrolysis temperature. In our previous study of pure iron catalyzed coal gasification, the mass fraction of iron was directly correlated to hydrogen yields [3]. However, the situation is complex for the coal gasification with FeCO₃–Na₂CO₃ composite catalysts. Higher loadings of iron generally produce higher yields of H₂, as indicated in Fig. 2, with the exception of the 3%-Fe + 1%-Na catalyst and coal mixture, which produced the least amount of hydrogen among the studied catalysts per mole of carbon in the char. This effect is apparently related to the higher rate of conversion of the 3%-Fe + 1%-Na mixture compared to the other composite ones, which was also observed during pyrolysis (see the previous discussion associated with Fig. 1). Much of the hydrogen formed during the gasification step was obtained from H₂O through the water-associated reactions, including the water gas shift (WGS) reaction. Table 2 shows the moles of H₂ per mole of C generated only from water. The coal loaded with the 4%-Fe + 0%-Na catalyst produced the highest amount of hydrogen. The hydrogen production at 800 °C increased from 1.25 mol H₂/mol C with raw coal to 1.45 mol H₂/mol C with the 4%-Fe + 0%-Na catalyst and coal mixture, a 16% increase. The 2%-Fe + 2%-Na and 1%-Fe + 3%-Na catalysts led to higher yields of hydrogen than the 3%-Fe + 1%-Na and the pure sodium catalysts did at a given temperature. For example at 800 °C, the production increased from 1.15 mol H₂/mol C with the 0%-Fe + 4%-Na catalyst and coal mixture to 1.32 mol H₂/mol C with the 2%-Fe + 2%-Na catalyst and coal mixture, a 15% increase. Metallic iron in the ash layer is reported to be the major driving force for hydrogen production [5].

The production of hydrogen with the Fe₂CO₃–Na₂CO₃ composite catalysts is lower than that of the coal with the pure iron catalyst (4%-Fe + 0%-Na). This is partially due to the presence of sodium ions during gasification, which can lower H₂ [2–5]. Temperature has an inverse effect on the yield of H₂ (see Fig. 2) as observed for non-catalyzed and catalyzed coal gasification [3,14]. As the gasification temperature increases, the composition of CO in the mixture starts to increase, and iron carbides and iron oxides become the only iron species present, which leads to the decrease in hydrogen production [3].

Figs. 3 and 4 show the molar yields of CO and CO₂ normalized per mole of carbon in the gasified char. In these figures, the production of CO and the CO/CO₂ ratio increase as the temperature increases. This fact has been studied in the past and can be related to the temperature dependence of the equilibrium constants of the water gas shift and the Boudouard reactions [3,4]. For the composite catalysts, the effect of higher loadings of iron and lower loadings of sodium was a decreased production of CO, except at 900 °C. At this temperature, the catalytic effect of both sodium and iron on these reactions is almost negligible [2–7]; therefore, the reported molar yields of CO were almost identical for the three catalysts. However, at 800 °C the use of composite catalysts led to a 53.4% increase in the production of CO compared to the one obtained with the use of pure iron catalyst (0.54 mol CO/mol C with the 4%-Fe + 0%Na catalyst and 0.83 mol CO/mol C with the 3%-Fe + 1%-Na catalyst). Sodium carbonate, as one component of the composite catalyst, also affects the gasification of the PRB coal [4]. In these reactions, the equilibrium favors the production of CO as the temperature increases [2,4,5,7]. On the other hand, the catalytic effect of iron on the reactions involved in the production of CO has been shown to be less extensive [4,5]. Furthermore, as the iron loading increases, the H₂/CO ratio increases as well, again with the exception of the 3%-Fe + 1%-Na composite catalyst, which

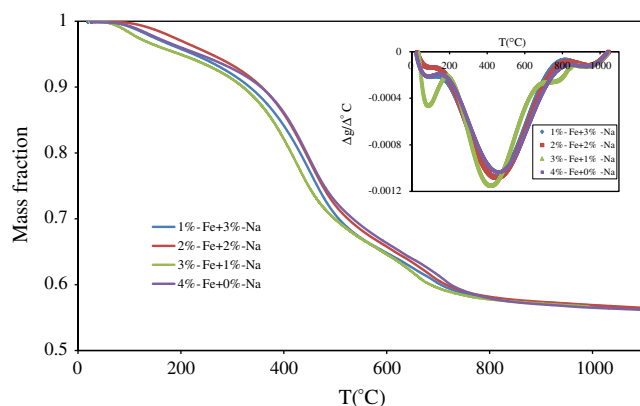


Fig. 1. TGA data for pyrolysis of coals loaded with different amount of composite catalysts.

Table 1
Ultimate analysis of the chars with composite catalysts.

Sample ID	Pyrolysis temperature	Ash (wt%)	C (wt%)	H (wt%)	N (wt%)	S (wt%)
4%-Fe + 0%-Na	700	18.19	79.00	1.09	1.21	0.51
4%-Fe + 0%-Na	800	16.57	81.22	0.76	1.40	0.36
4%-Fe + 0%-Na	900	16.09	81.83	0.44	0.95	0.73
3%-Fe + 1%-Na	700	16.79	80.39	1.08	1.26	0.47
3%-Fe + 1%-Na	800	15.75	82.11	0.56	1.19	0.38
3%-Fe + 1%-Na	900	13.26	85.33	0.15	0.82	0.44
2%-Fe + 2%-Na	700	16.12	81.30	0.94	1.33	0.32
2%-Fe + 2%-Na	800	15.79	82.03	0.62	1.10	0.47
2%-Fe + 2%-Na	900	13.90	84.14	0.29	1.08	0.58
1%-Fe + 3%-Na	700	15.31	82.03	0.94	1.47	0.25
1%-Fe + 3%-Na	800	13.78	83.93	0.65	0.97	0.67
1%-Fe + 3%-Na	900	13.52	84.91	0.21	1.05	0.30

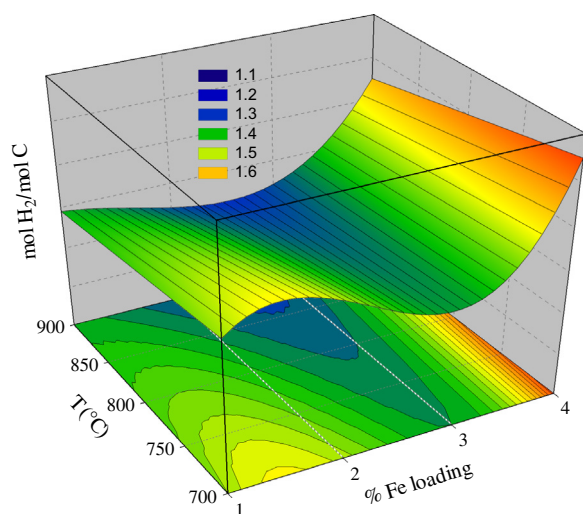


Fig. 2. Molar yields of H_2 per mole of carbon in the char vs. loadings of Fe and gasification temperatures [Numbers 1, 2, 3 and 4 in the Fe loading axis represent 1%-Fe + 3%-Na, 2%-Fe + 2%-Na, 3%-Fe + 1%-Na, and 4%-Fe + 0%-Na, respectively].

Table 2
Molar yield of H_2 (H_2 /mol C in char) that originated from H_2O .

T (°C)	1%-Fe + 3%-Na	2%-Fe + 2%-Na	3%-Fe + 1%-Na	4%-Fe + 0%-Na
700	1.32	1.33	1.22	1.48
750	1.27	1.23	1.22	1.43
800	1.16	1.23	1.07	1.38
850	1.13	1.22	1.09	1.33
900	1.12	1.18	1.09	1.17

is related to the decreased production of H_2 with this catalyst as discussed previously in association with Fig. 2 and Table 2.

3.2.2. Time

Fig. 5 shows the trend of H_2 production as a function of time at different temperatures for the two pure and three composite catalysts and coal mixtures evaluated. Although at 700 °C the highest observable value corresponds to the 0%-Fe + 4%-Na catalyst, this is only due to the initially increased reaction rate with pure sodium catalyst loaded coals, since as the time proceeds, the overall production of H_2 is lower than that of the composite catalysts and the pure iron catalyst. This effect is more evident as the temperature increases, since at 900 °C (Fig. 5c), when the reaction is complete, the overall yield of hydrogen with this catalyst is the lowest. Nonetheless, the effect of sodium in the composite catalysts is not completely undesirable, as it is an aid in accelerating hydrogen

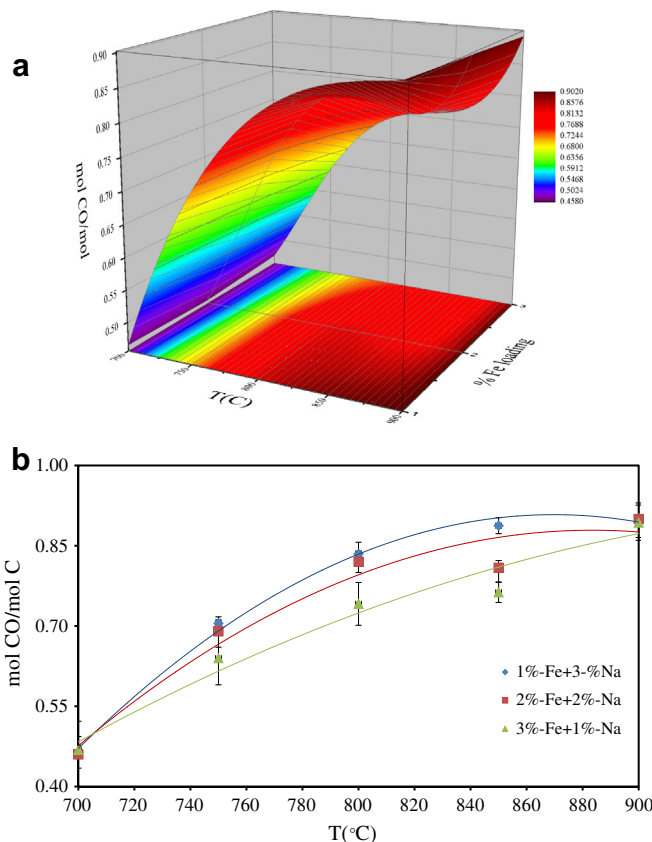


Fig. 3. Molar yield of CO per mole of carbon in the char vs. different loadings of Fe and temperatures, (a) average molar yield of CO, (b) average molar yield of CO with error bars [numbers 1, 2 and 3 in the Fe loading axis represent 1%-Fe + 3%-Na, 2%-Fe + 2%-Na, and 3%-Fe + 1%-Na, respectively].

production. These catalysts lead to faster hydrogen generation rates than pure iron catalysts do. Therefore, an interesting balance between the production rate of hydrogen and the overall yield is obtained when using composite catalysts. In this case, the 2%-Fe + 2%-Na catalyst demonstrates considerable advantages, as it produces hydrogen at a faster rate than the other composite catalysts, while being slower than the pure sodium catalyst only during a few stages of the reaction at different temperatures. In the case of the 3%-Fe + 1%-Na catalyst, the results demonstrate again a reduced yield of hydrogen compared to the other composite catalysts. In general, the effect of composite catalysts is superior in terms of efficiency and total yield in production of hydrogen when compared to pure iron or pure sodium catalysts.

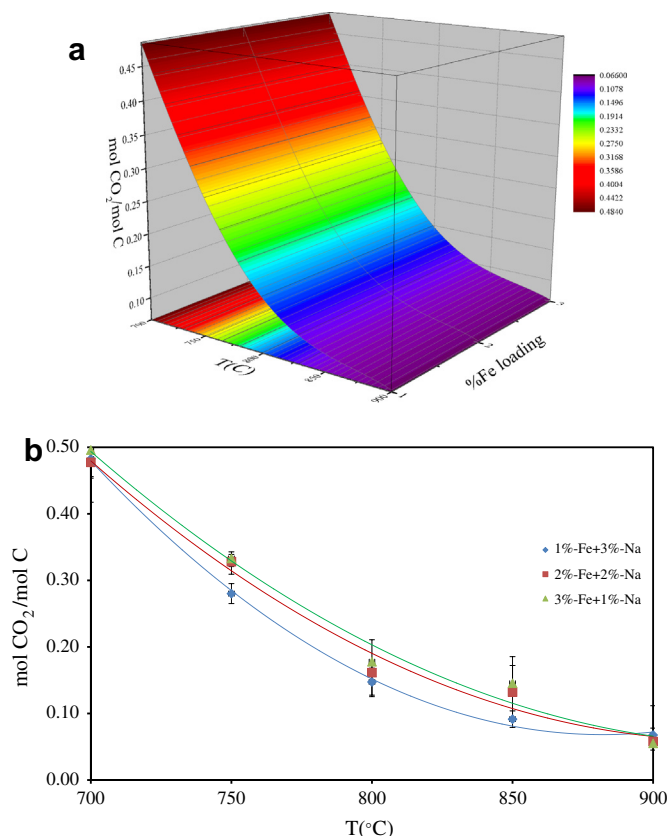


Fig. 4. Molar yield of CO_2 per mole of carbon in the char vs. different loadings of Fe and gasification temperatures, (a) average molar yield of CO_2 (b) average molar yield of CO_2 with error bars [numbers 1, 2 and 3 in the Fe loading axis represent 1%-Fe + 3%-Na, 2%-Fe + 2%-Na, and 3%-Fe + 1%-Na, respectively].

Fig. 6 shows the trend of CO production as a function of time at different temperatures for the tested catalyst and coal mixtures. The rates and overall yields of CO increase with sodium concentration of either the pure catalysts or the composite catalysts. The composite catalysts showed a notable advantage in terms of CO production rates over the pure iron catalyst (4%-Fe + 0%-Na), while the primacy in terms of the overall efficiency was obtained with the pure sodium catalyst (0%-Fe + 4%-Na). The mechanisms through which Na_2CO_3 enhances the rate and the overall production of CO include the oxidation step of carbon through Na_2O and a subsequent reduction of CO_2 by metallic sodium [6,17,18]. Saber and Falconer noticed that other carbon oxidizers could also exist during sodium-based catalytic coal gasification [19], which was confirmed by Certofontain et al. [18,20,21] who found that alkali phenolates and oxygen deficient alkali oxides were carbon oxidizers. These types of complexes might not exist when iron-based catalysts are being used, and thus iron catalysts have less positive impact on CO production than sodium.

3.3. Effects of catalysts on carbon conversion kinetics

3.3.1. Conversion

Fig. 7 shows the coal conversion plots at 700 $^{\circ}\text{C}$, 800 $^{\circ}\text{C}$, and 900 $^{\circ}\text{C}$, in which the enhanced carbon conversion rates for all of the catalysts, especially of the 3%-Fe + 1%-Na catalyst during the gasification process, are evident relative to the uncatalyzed gasification. The effect of the catalysts is particularly pronounced at the lower reaction temperatures, where the conversion of carbon in raw coal is considerably slower than that of the catalyzed coals. Obviously, use of the catalysts can reduce the gasification

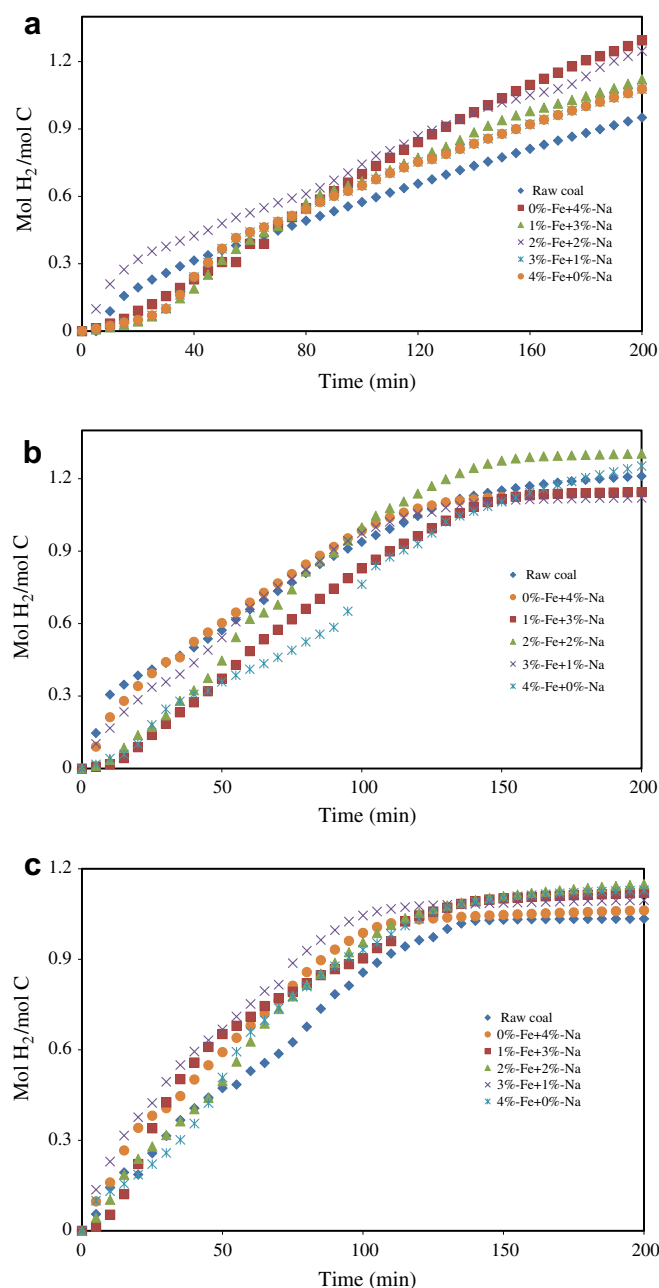


Fig. 5. Effect of time on H_2 production at (a) 700 $^{\circ}\text{C}$, (b) 800 $^{\circ}\text{C}$, and (c) 900 $^{\circ}\text{C}$ for different composite and pure catalysts.

temperature. The 4%-Fe + 0%-Na catalyst shows better performance in terms of conversion rate compared to the raw coal at 700 $^{\circ}\text{C}$; nevertheless, as the gasification temperature increases, the improvement is hindered, especially in the later period of gasification, as observed in Fig. 7b and c, in which raw coal displays a higher slope during this portion. This effect can be directly explained by the proposed iron-catalyzed coal gasification mechanism in which metallic iron in the form of γ -Fe can be present, but has no catalytic effect due to its lack in mobility in the ash layer; furthermore, if cementite (Fe_3C) is still present at such temperatures, the catalytic effect disappears since iron carbides are inert species and will only make the overall gasification process slower by creating mass transfer resistance [3,4]. Conversely, the 0%-Fe + 4%-Na catalyst presents higher conversions rates at all temperatures. The composite catalysts show the previously

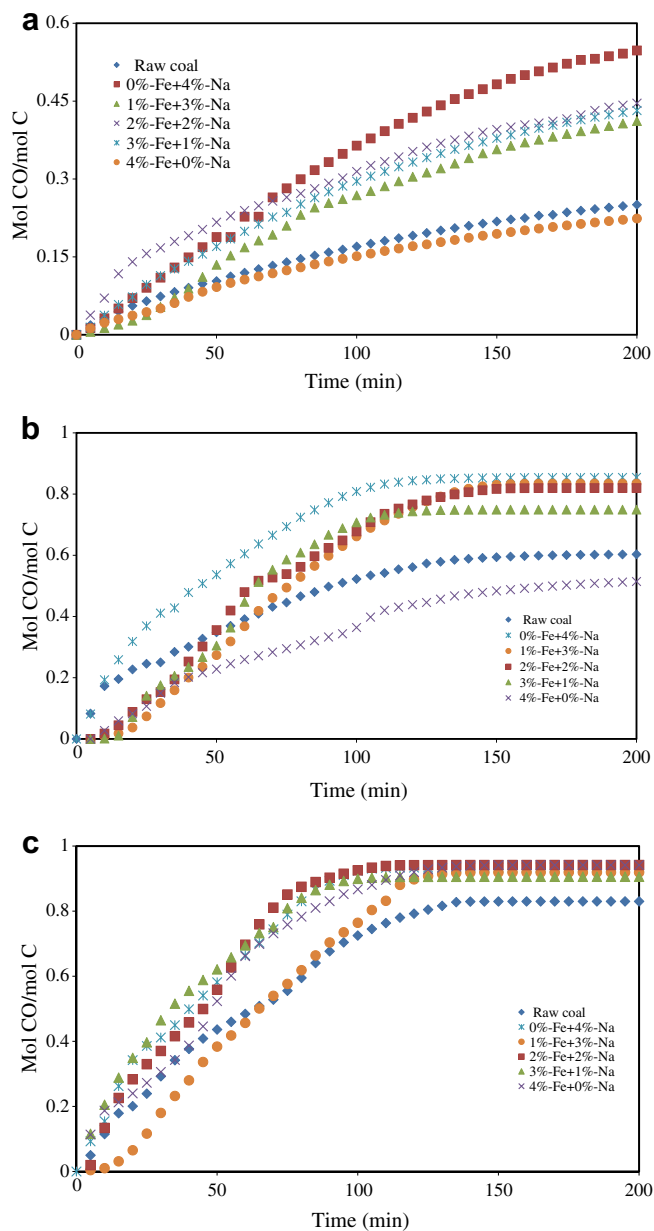


Fig. 6. Effect of time on CO production at (a) 700 °C, (b) 800 °C, and (c) 900 °C for different composite and pure catalysts.

discussed trend, in which the 3%-Fe + 1%-Na catalyst demonstrates a higher carbon conversion rate that is even more evident as the temperature increases. At 700 °C, the effect of this catalyst is fairly similar to those of the other composite catalysts. Thus, conversion appears to be fairly insensitive to the composition of the iron and sodium catalysts for gasification at this lower temperature, so the optimal Fe to Na ratio should be selected to achieve desired gas yields or tar mitigation capability. Some results in terms of tar alleviation capabilities by composite catalysts were observed, however the data and analysis of the mitigation mechanism will be published in a different study. At 800 °C and 900 °C, the effect of 3%-Fe + 1%-Na catalyst, is considerably more pronounced; at 800 °C, the carbon conversion is faster than those obtained with the other two composite catalysts; and at 900 °C, the conversion rate is better than even that of 0%-Fe + 4%-Na during the earlier period of gasification. It is hypothesized that this behavior is related to an enhanced mobility of the catalytic iron species when sodium is

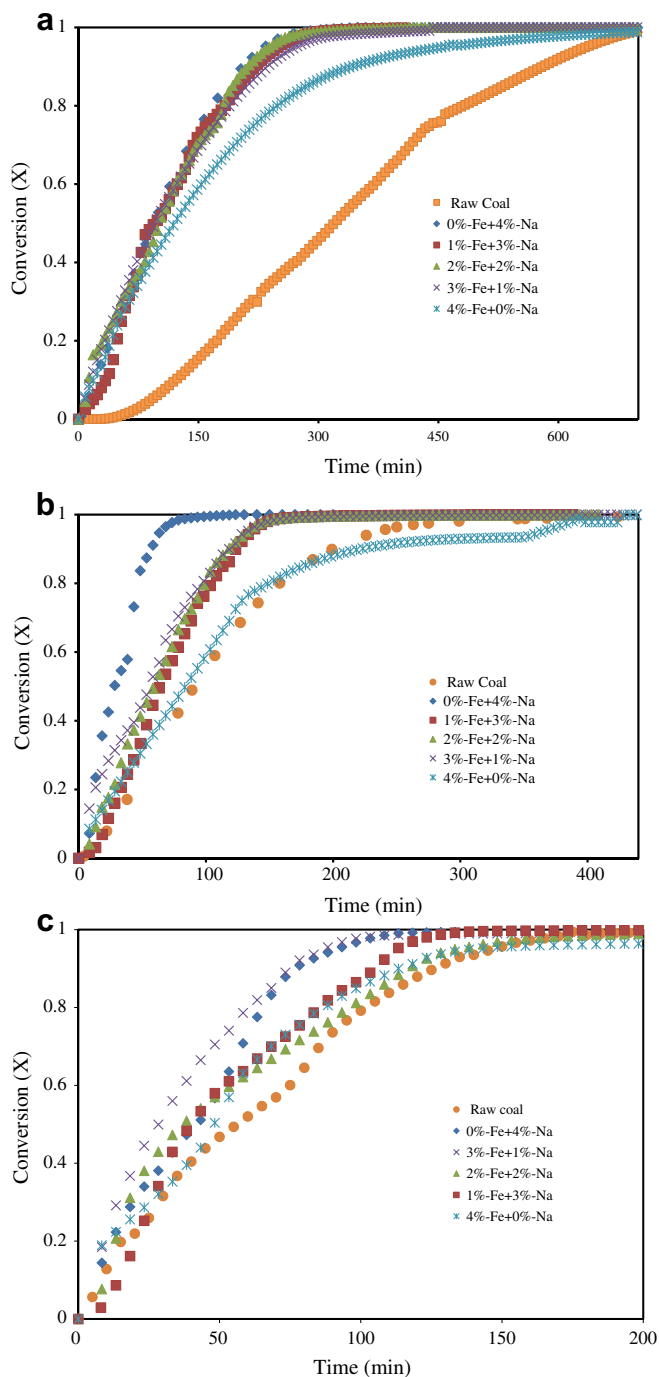


Fig. 7. Conversion vs. time for different composite catalysts, pure catalysts and raw coal at (a) 700 °C, (b) 800 °C and (c) 900 °C.

present. Current studies are being conducted to investigate this claim. Hematite and α -Fe, which play an important role during the latter stages of the gasification process [3], could be activated due to the presence of metallic sodium ions [4,6]. This is consistent with the reaction rate constants discussed next and the results obtained by Popa et al. [2,3] when using different compositions of sodium or iron as single catalysts. Further evidence of these effects has previously been described in the devolatilization rates observed during the pyrolysis stage shown in Fig. 1.

3.3.2. Shrinking core model

The gasification kinetics were quantified in the 700–900 °C temperature range. The shrinking core model was used to

represent the coal gasification kinetics studied in this research. The shrinking core model [22–25] is based upon the following equation:

$$-\frac{dX}{dt} = k_{sc}(1-X)^{2/3} \quad (E1)$$

where X is the carbon conversion fraction, t is time, and k_{sc} is the specific carbon conversion rate constant.

The model assumes that the overall rate is essentially equal to the observed rate of reaction, while the diffusivity rate constant can be neglected. According to the literature, diffusion resistances for gasification products (CO and H_2) are negligible [26,27]. In the first stage, the coal particle has a film boundary layer through which steam diffuses to the surface to react with carbon. For the composite catalytic coal gasification, species such as Fe_3O_4 and Na_2CO_3 are predominantly present on the carbon surface and thus influence the reaction between carbon and water vapor [3,4]. Temperature, composition of reaction products including CO , and concentrations of the catalytic species such as FeO and Na_2O play important roles at the beginning of gasification [6]. Subsequently, the reaction moves from the surface into the particle through a layer of ash and catalyst, to the interface of the shrinking, unreacted core that progresses toward the center of coal particle [26]. This movement is assumed to occur uniformly. Thus, a reduction of the char particle radius must take place as gasification advances, since at this point of the catalytic gasification reaction, most of the gaseous products are formed. The reaction rate decreases when the gasification nears completion at the core because active sites on char particle become less available and shrinking core model cannot accurately represent the gasification kinetics [26,27]. Therefore, E1 was only applied to fit the data collected during the initial stages of the gasification process, which analytically was during the linear portion of the conversion vs. time curves. The shrinking core model does not account for conditions near the end of the reaction, such as the decrease of reactants near the iron and low mobility of some of the catalytic agents such as Fe^0 [3], and therefore it cannot be applied to the nonlinear part of the conversion.

3.3.3. Rate constants

The values of the reaction rate constant (k_{sc}) derived from E1 under different catalytic gasification conditions are listed in Table 3. The rate constants increase as a result of the use of the composite catalysts. They do not necessarily change linearly with the concentrations of sodium and iron, which is a confirmation of our previous finding that pure iron catalysts enhance the rate of the reaction only through a portion of the process as conversion progresses, while pure sodium based catalysts increase the reaction rate over the entire range. The kinetics improvement of iron catalyzed gasification. The improvement of the kinetics of iron catalyzed coal gasification when sodium is present in composite catalysts is reflected in the corresponding k_{sc} values. For example, at 800 °C, the k_{sc} value for the 4%-Fe + 0%-Na catalyst is only 0.0022 min^{-1} , while that for the 3%-Fe + 1%-Na catalyst is 0.0044 min^{-1} , a 100% improvement. At 700 °C, the use of the 3%-Fe + 1%-Na composite catalyst increased the conversion rate

constant from 0.0012 min^{-1} with raw coal to 0.0022 min^{-1} , an increase of 1.83 times. At 800 °C, the improvement is 1.5 times for this catalyst (0.0044 min^{-1} vs. 0.0029 min^{-1} obtained for raw coal). Moreover, the rates of reaction are considerably higher in the case of the pure sodium catalyst and coal mixture (0%-Fe + 4%-Na) compared to those of raw coal, whereas some of the reaction rates of the pure iron catalyst and coal mixture (4%-Fe + 0%-Na) are lower than those of raw coal. Therefore, when iron and sodium are present together during gasification, they may function synergistically through the possible formation of sodium ferrites ($\text{Na}_x\text{Fe}_y\text{O}_z$) or similar complexes at particular compositions of the catalysts. The synergy may exist in different ways. Another possibility, as it was previously mentioned, is that the catalytic effect of iron on coal gasification may be enhanced by its coexistence with sodium due to the function of the latter in improving the mobility of iron. This study is being conducted separately by the research group and the results will be published separately.

Fig. 8 shows the Arrhenius plots for the carbon conversions accelerated by the composite catalysts. The comparisons of carbon conversion reaction rate constants indicate that the 3%-Fe + 1%-Na catalyst is better than the 2%-Fe + 2%-Na and 1%-Fe + 3%-Na ones. The superiority of the 3%-Fe + 1%-Na catalyst when compared to the 2%-Fe + 2%-Na catalyst is not fully evident in Fig. 8a because during the first stage of the reaction through which the shrinking core model is applicable, the difference between these two catalysts is trivial. At higher temperatures, raw coal is superior to the pure-iron catalyst (4%-Fe + 0%-Na) (Fig. 8c), which is also being investigated in the previously mentioned ongoing research. Certofontaine et al. [18] stated that the rate determining step of the alkali metals based catalytic coal gasification mechanism is the decomposition of an intermediate carbon oxygen surface species, which refers to R6 for the case of the sodium catalyzed gasification. However, Suzuki et al. [4,6] demonstrated that when using this type of composite catalyst, the rate determining step is the oxygen transfer from the metal oxide species, namely Na_2O and Fe_3O_4 . The increased oxygen transfer in the case of Fe_3O_4 could be a result of the enhanced mobility created by the presence of metallic sodium; consequently an improvement in the reaction rates of R6 through R9 is expected.

Based on the results shown in Table 3, sodium increases the gasification rate more significantly than iron because the k_{sc} values obtained with 3%-Fe + 1%-Na are always higher than those with 4%-Fe + 0%-Na. The rate constants achieved with all the composite catalysts are not only higher than those without catalysts (the raw PRB coal) but also those with pure iron catalysts. They are lower than those with pure sodium catalysts in the temperature range of 700–850 °C, but this relative difference decreases with temperature. For example, at 700 °C, the rate constant with 2%-Fe + 2%-Na is about 42% higher than that with the 4%-Fe + 0%-Na, while the difference is about 30% at 900 °C.

3.3.4. Activation energies

A decrease in the activation energies with the use of any of the studied catalysts was observed when compared to the result exhibited by raw coal. The composite catalysts reduce the activation energy of carbon conversion by ~30–40%. The activation

Table 3
Carbon conversion reaction rate constants (min^{-1}) obtained from the shrinking core model.

T (°C)	0%-Fe + 4%-Na	1%-Fe + 3%-Na	2%-Fe + 2%-Na	3%-Fe + 1%-Na	4%-Fe + 0%-Na	Raw coal
700	0.0028	0.0018	0.0020	0.0022	0.0014	0.0009
750	0.0045	0.0027	0.0033	0.0032	0.0022	0.0015
800	0.0052	0.0032	0.0046	0.0044	0.0028	0.0029
850	0.0058	0.0047	0.0052	0.0049	0.0041	0.0037
900	0.0072	0.0057	0.0064	0.0071	0.0049	0.0060

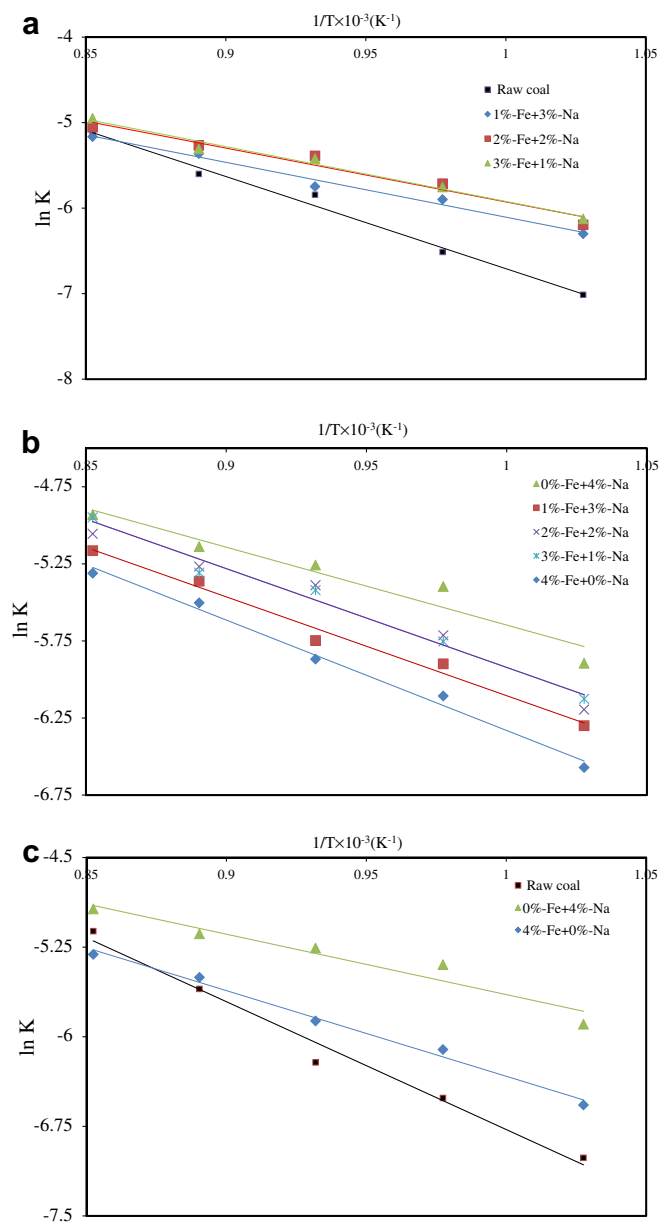


Fig. 8. Arrhenius plots: (a) 3 composite catalysts and raw coal, (b) Iron and sodium pure catalysts and raw coal and (c) Pure iron and sodium catalysts and composite catalysts.

energy obtained with non-catalytic coal gasification was 89.0 kJ/mol, which was reduced to ~52 kJ/mol with the use of the 2%-Fe + 2%-Na catalyst. For the other catalysts, the activation energies generally increased with increasing iron content and decreasing sodium content, as follows: $E_{a0\%-Fe+4\%-Na} = 42.0$ kJ/mol, $E_{a1\%-Fe+3\%-Na} = 53.3$ kJ/mol, $E_{a2\%-Fe+2\%-Na} = 53.4$ kJ/mol and $E_{a4\%-Fe+0\%-Na} = 59.6$ kJ/mol. The Arrhenius equation is

$$k_{sc} = Ae^{-E_a/RT} \quad (E2)$$

where A is the pre-exponential factor, R is the ideal gas constant, and T is the absolute reaction temperature. Analysis of this equation indicates that use of catalysts, including composite ones, leads to small decreases in the pre-exponential factor. However, the net effects of the catalysts on the PRB coal gasification are positive at

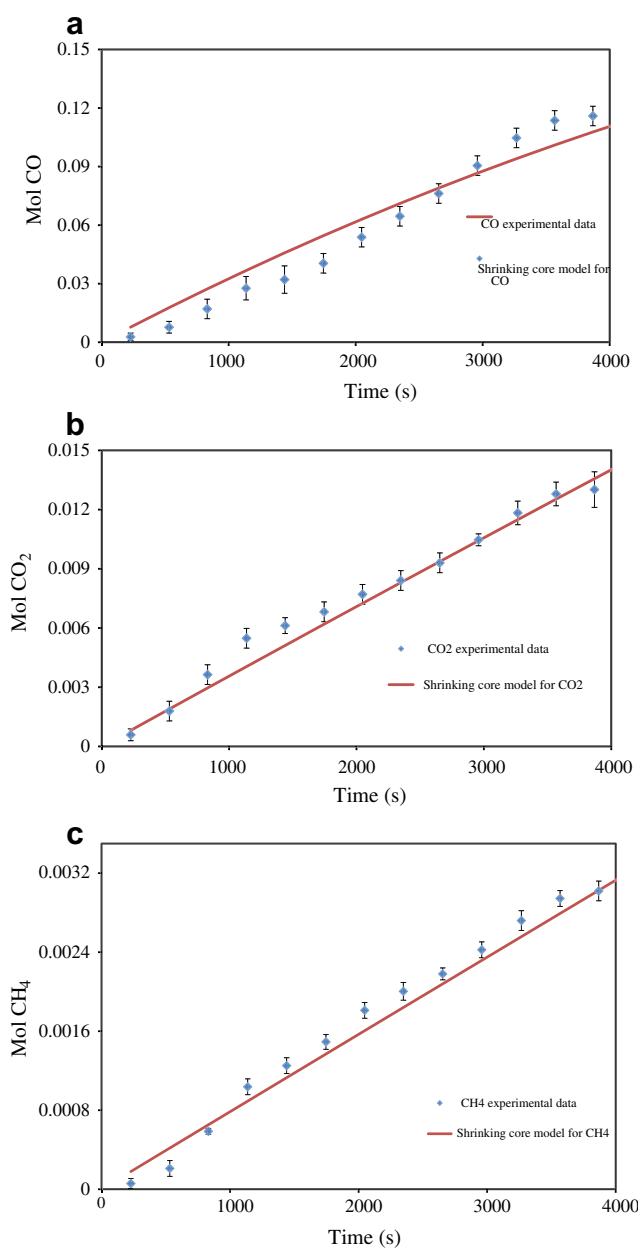


Fig. 9. Carbonaceous gas yielding data fitting for a 2%-Fe + 2%-Na catalyst and coal mixture (a: CO; b: CO₂; c: CH₄) with extended shrinking core model at 800 °C.

most of the tested temperatures due to their roles in significant reductions of the activation energy.

3.3.5. Application of the shrinking core model to the yields of individual carbonaceous products

The shrinking core model is typically used to derive particle associated reaction kinetics. In this research, this use was expanded to also model the yield of each carbon-containing gas species as follows. Conversion, X_i ($i = \text{CO}, \text{CO}_2, \text{CH}_4$), is defined as

$$X_i = \frac{N_{i,t}}{N_{i,f}} \quad (E3)$$

where $N_{i,t}$ refers to the moles of carbonaceous gas, i , generated or moles of carbon converted to produce the carbonaceous gas, i , at any time and $N_{i,f}$ refers the total moles of carbonaceous gas generated or the total moles of carbon converted to produce the

carbonaceous gas at the end of the gasification. Combining E1 and E3 leads to:

$$-\frac{d\left(\frac{N_{i,t}}{N_{i,f}}\right)}{dt} = k_{sc,i} \left(1 - \frac{N_{i,t}}{N_{i,f}}\right)^{2/3}. \quad (\text{E4})$$

The integral form of E4 is

$$N_{i,t} = \left[1 - \left(-\frac{k_{sc,i}t}{3} + 1\right)^3\right] * N_{i,f} \quad (\text{E5})$$

or

$$\left(\frac{N_{i,f} - N_{i,t}}{N_{i,f}}\right)^{\frac{1}{3}} = -\frac{k_{sc,i}}{3}t + 1 \quad (\text{E6})$$

where $k_{sc,i}$ is the generation rate constant of species i . E6 was used to model the yields of CO, CO₂, and CH₄ from the 2%-Fe + 2%-Na catalyzed PRB coal gasification process at 800 °C. The results of the model for each of the three gases compared with the experimental data are shown in Fig. 9. The resulting generation rate constants are $k_{sc,CO} = 1.56 \times 10^{-4} \text{ s}^{-1}$, $k_{sc,CO_2} = 1.63 \times 10^{-5} \text{ s}^{-1}$, and $k_{sc,CH_4} = 3.57 \times 10^{-6} \text{ s}^{-1}$. The model fits are reasonable based on the regression coefficients of the three plots, as the coefficients of determination are $r_{CO}^2 = 0.9469$, $r_{CO_2}^2 = 0.9999$, and $r_{CH_4}^2 = 0.9782$. E6 was not used to model hydrogen production data because the majority of the hydrogen produced comes from water instead of coal or char.

4. Conclusions

The rates of carbon conversion during gasification of Wyodak PRB coal were considerably improved under different conditions by using the composite catalyst (FeCO₃–Na₂CO₃) when compared to those obtained from raw coal or the pure iron catalyst. The use of the composite catalyst FeCO₃–Na₂CO₃ during coal gasification can improve the yields of useful gases, including hydrogen and carbon monoxide. The composite catalyst appears to combine the advantages of its two component catalysts and to overcome their individual shortcomings. Therefore, FeCO₃–Na₂CO₃ composite catalysts are promising materials for catalytic coal gasification, although more work needs to be performed before the feasibility becomes a reality.

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