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1-1-2014

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Brian Monaghan

University of Wollongong, monaghan@uow.edu.au

Apsara Jayasekara

University of Wollongong, asj945@uowmail.edu.au

Raymond Longbottom

University of Wollongong, rayl@uow.edu.au

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Abstract

A coke analogue has been developed to evaluate mineral effects on coke reactivity. Elucidation of the effects of minerals on coke reactivity has proved difficult due to the complex and heterogeneous nature of industrial coke and the potential non-additive effects of minerals on coke reactivity. The coke analogue addresses this complexity and heterogeneity through control of its mineralogy, porosity and carbon structures. Recent studies have shown the analogue is capable of discriminating individual mineral effects on coke reactivity. In this paper the reaction mechanism of the analogues reactivity in CO₂ is assessed and compared with that of industrial coke.

Keywords

mineral, approach, novel, coke, effects, reactivity

Disciplines

Engineering | Science and Technology Studies

Publication Details

Monaghan, B. J., Jayasekara, A. J. & Longbottom, R. J. (2014). A novel approach to mineral effects on coke reactivity. Innovation of Ironmaking Technologies and Future International Collaboration to Overcome Energy & Resource Restrictions in Accordance with Environments (pp. 149-156). Japan Society for Promotion of Science.

A Novel Approach to Mineral Effects on Coke Reactivity

Brian J. Monaghan^a, Apsara S. Jayasekara^a, Ray J. Longbottom^a

^a*Engineering Materials Strength and School of Mechanical Materials and Mechatronics, University of Wollongong, Northfield Ave, Wollongong, NSW 2522, Australia*

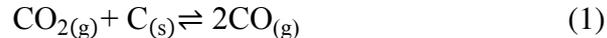
Abstract:

A coke analogue has been developed to evaluate mineral effects on coke reactivity. Elucidation of the effects of minerals on coke reactivity has proved difficult due to the complex and heterogeneous nature of industrial coke and the potential non-additive effects of minerals on coke reactivity. The coke analogue addresses this complexity and heterogeneity through control of its mineralogy, porosity and carbon structures. Recent studies have shown the analogue is capable of discriminating individual mineral effects on coke reactivity. In this paper the reaction mechanism of the analogues reactivity in CO₂ is assessed and compared with that of industrial coke.

Keywords: Coke combustion, reactivity, reaction mechanisms, Boudouard reaction, coke kinetics, TGA

1. Introduction

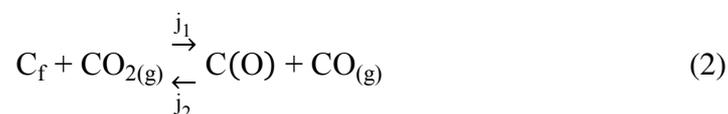
Coke combustion in CO₂ is critical to understanding coke's reaction behavior in metal production and power generation. The reaction of coke in CO₂ may be represented by equation 1



and is often referred to in the literature as the Boudouard reaction, solution loss reaction or even coke gasification [1].

Coke has a complex structure made up of different maceral groups (carbon forms) and minerals and has a highly variable porous structure. Further, it often displays significant heterogeneity in key characteristics such as its maceral grouping, mineralogy, phase dispersion, morphology and porosity. This complexity and heterogeneity often mask crucial reaction behavior, making it difficult to isolate specifics of minerals or carbon type or porosity on coke reactivity. A coke analogue has been developed using laboratory grade materials (graphite, Bakelite, Novolac and minerals) for use in examining coke reactivity to address these complexity and heterogeneity issues of industrial cokes. Use of the coke analogue offers control in the selection and combination of minerals, mineral particle size and dispersion, and analogue porosity. The analogue has been used in studies replicating coke dissolution behavior in iron [2,3], in studies of individual effects of minerals on coke combustion in CO₂ [4,5] (see Figure 1) and its combustion properties are currently being validated for industrial cokes. A current focus of the coke analogue work is to assess whether the coke analogue kinetics are similar to that of industrial coke.

While equation 1 represents the overall combustion reaction, from a mechanistic perspective it is better represented by a two-step reaction sequence given in equations 2 and 3





where j_1 , j_2 and j_3 are rates of reaction, C_f an active carbon site and $C(O)$ chemisorbed oxygen on carbon. In the first step (equation 2), an oxygen exchange reaction [6,7], CO_2 dissociates into CO forming an oxidized surface complex $C(O)$. In the second step (equation 3), the surface oxygen complex produces another CO molecule leaving a free C_f for further reaction. The second step is the slowest [7]. The rates of the forward and backward reactions of equation 2 are very rapid and the CO and CO_2 are considered to be in equilibrium [8,9].

Using an Arrhenius approach to studying coke combustion kinetics (equation 4), previous workers [8,10,11,12,13] have established three distinct rate controlling regimes,

$$\text{Rate} = k_0 \exp \left(- \frac{E}{RT} \right) \quad (4)$$

where k_0 is a pre-exponential constant, E is an activation energy, R is the gas constant and T is temperature.

These three zones are shown schematically in Figure 2.

Zone I is the low temperature chemical reaction controlled zone, where the rate is controlled by the chemical reaction at solid-gas interface. Zone II, the intermediate temperature zone, is a mixed control region where both chemical reaction at the solid-gas interface and pore diffusion are active. In zone III, the high temperature zone, the rate is controlled by the mass transfer in the gas phase to the external solid surface [10,14]. The areas (a) and (b) in Figure 2 represent transition regions between the different zones. The transition temperatures are at least in part a function of coke material [8,11,14,15,16,17,18] though other factors such particle size, porosity, the number of active carbon sites, gas flow rate, gas type and gas pressure can also have an effect [8,11, 14,15,16].

In this paper the preliminary results of a thermo-gravimetric (TGA) study into the kinetics of coke analogue combustion in CO_2 are presented/discussed.

2. Experimental

TGA combustion experiments were carried out over the temperature range 1173-1623 K in CO_2 gas. The system was heated at $10^\circ C/min$ to the desired temperature under Ar at gas flow rate of 1 L/min. The gas was then switched to CO_2 at a flow rate of 4.5 L/min for 2 hours. Both gases were high purity 99.99% cleaned by passing through drierite and ascarite. The Ar was further cleaned with Cu turnings at 573 K. See Figure 3 for a schematic of the experimental set up used. After 2 hours the CO_2 was switched off and the sample cooled down under argon. Weight change during the reaction is logged to a PC. From these measurements the fractional weight change (FWC) and the rate of reaction (R_C) were calculated using equations 5 and 6 respectively,

$$FWC = (W_f - W_o) / W_o \quad (5)$$

$$R_C = (1/W_o) \times (dW/dt) \quad (6)$$

where W is mass, t is time and the subscripts f and O denote final and initial respectively.

The coke analogue was prepared from mixtures of graphite, Novolac resin, bakelite and hexamethylenetetramine (HTMA) and fired under Argon at 1473 K. Full details of the preparation procedure are given elsewhere [5].

3. Results and Discussions

The results of the TGA CO_2 combustion experiments are given in Figures 4 and 5 for FWC and $\ln R_C$ respectively. Both final FWC and $\ln R_C$ increased with increasing temperature. It is known and also shown in equation 6, that the CO_2 combustion process is a temperature activated reaction. The results given in Figures 4 and 5 are consistent with this. A similar trend has been observed and reported for industrial coke and char [19,20].

In Figure 4 for the highest temperature (1623K) experiment, there appears to be a flattening of the curve with respect to FWC at ~6000s i.e. the FWC is constant after this time. There was little left of the analogue after the test. This flattening or constant FWC is likely a result of complete combustion of the carbon in the analogue after approximately 6000s.

In Figure 5, the results are plotted in an Arrhenius form that aids identification of the reaction mechanism of the analogue combustion in CO_2 . When compared with Figure 2, a schematic showing the three distinct reaction zones for industrial coke, it can be seen that there appears to be good agreement. This would indicate that the coke analogue is showing similar reactivity behavior in CO_2 as that of industrial coke. This is likely to indicate similar reaction mechanisms are active in the analogue. This is an important finding showing the analogue appears to be able to represent the reactivity behavior of industrial coke. On that assumption, the transition temperatures from zone I to zone II and zone II to zone III have been identified as ~1298K and ~1423K respectively.

Much of the published work on CO_2 reactivity with coke has been carried out in zone I the low temperature range. The relative abundance of data in this zone offers a useful comparison of analogue and industrial coke reactivity.

The measured rates of reaction from the low temperature region (region I) are compared against the literature [8,12,14,21] in Figure 6. From this figure it can be seen that the industrial cokes and the coke analogue have similar reactivity characteristics with changing temperature, though the analogue had, in general, a lower reaction rate than those reported for the industrial cokes. There are a number of factors that could explain this lower reaction rate. It is known that the number of active carbon sites affects the rate of reaction [10]. Further, the formation of these carbon active sites is known to be related to minerals, maceral size and type and micro-texture of the coke. The coke analogue used in this study has no mineral component, has a more controlled but finer pore structure and lower overall porosity than is generally found in industrial cokes. It is likely one or a combination of these factors that have resulted in the lower reactivity value. Previously reported work has shown that the addition of minerals can change the reactivity of the coke analogue [4,5] (See Figure 1). The control of the mineral addition in the analogue offers a degree of controllability of the reactivity of the analogue and offers the possibility of testing

specific effects of mineralogy on analogue reactivity. Further research is currently underway assessing these effects.

4. Conclusions

A coke analogue has been developed that shows similar combustion behavior in CO₂ to that of industrial coke. Further, and again similar to that of industrial coke, over the temperature range 1173-1623 K, three different reaction control regions have been established corresponding to chemical reaction control (zone I), chemical reaction and pore diffusion control (zone II), and mass transfer control (zone III). Though similar, the reactivity of the coke analogue was generally lower than that for industrial cokes. This lower reactivity of the coke analogue is thought to be a result of a combination of factors relating to the absence of minerals in the analogue and different (finer and lower) total porosity of the coke analogue.

The similarity of the kinetics of combustion of the analogue in CO₂ with that of industrial coke offers possibilities of identifying and understanding specific mineral effects on the reactivity or in use behavior of industrial coke.

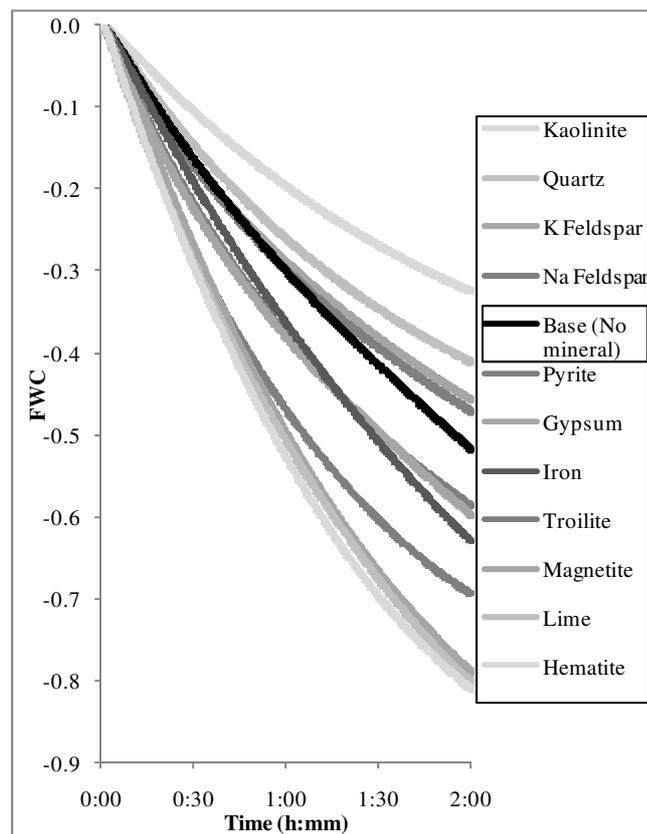


Figure 1. Changes in fractional weight change (FWC) with time for single mineral containing coke analogues in CO₂ gas at 1100°C [4]. Note the legend lists the minerals in their order of reactivity from lowest (top) to highest (bottom). The mineral concentration in the analogues was 0.1 mol. of cations per 100g of carbonaceous material after firing.

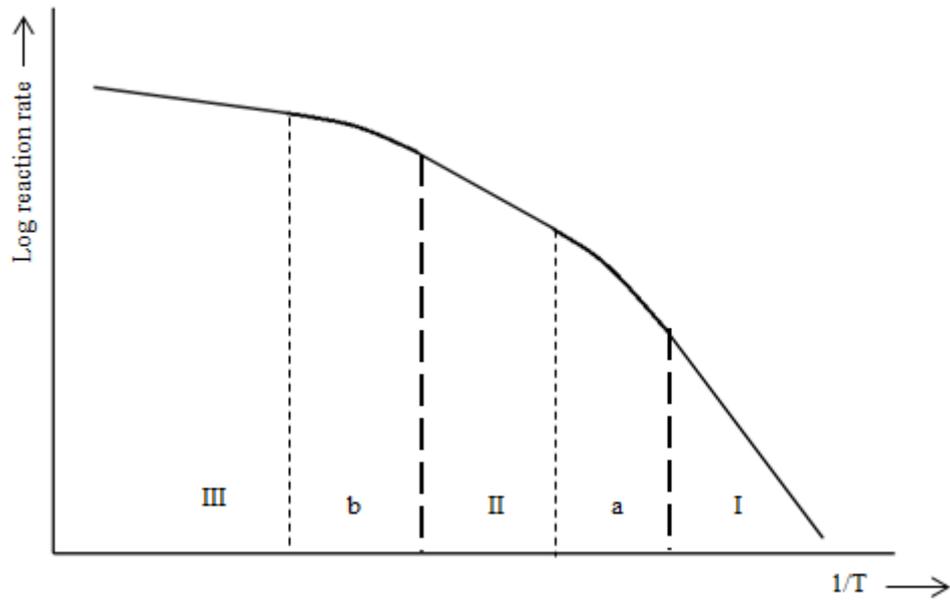


Figure 2. A Schematic of the effect of temperature on the reaction control mechanism of coke combustion in CO_2 gas.

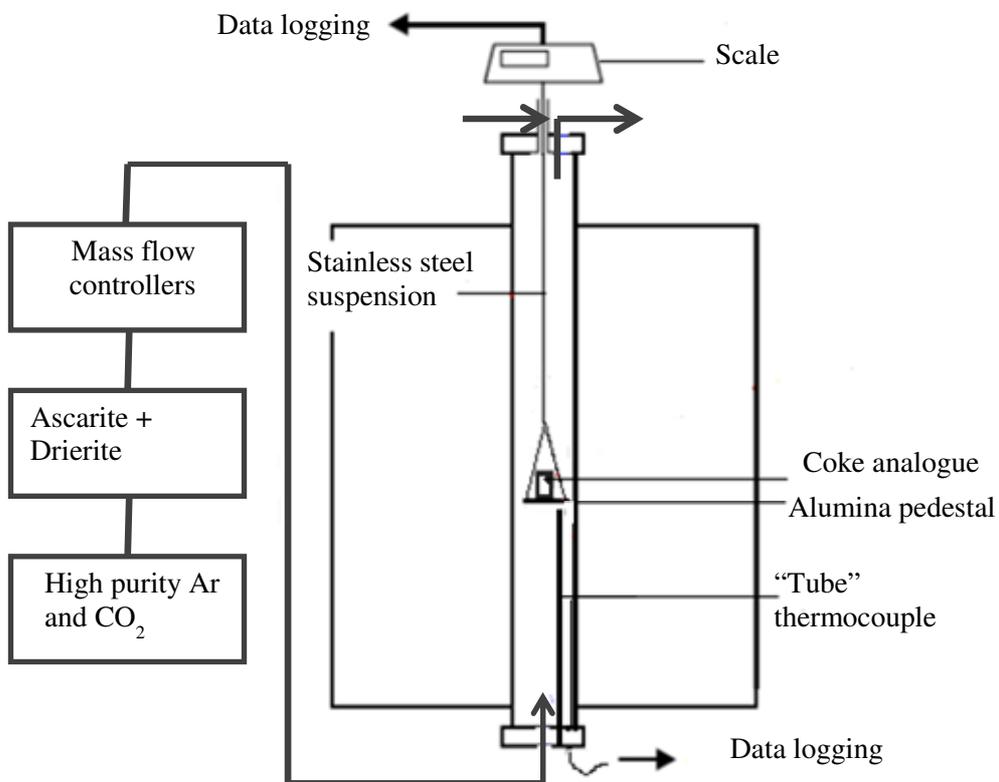


Figure 3. A schematic of the TGA experimental set up.

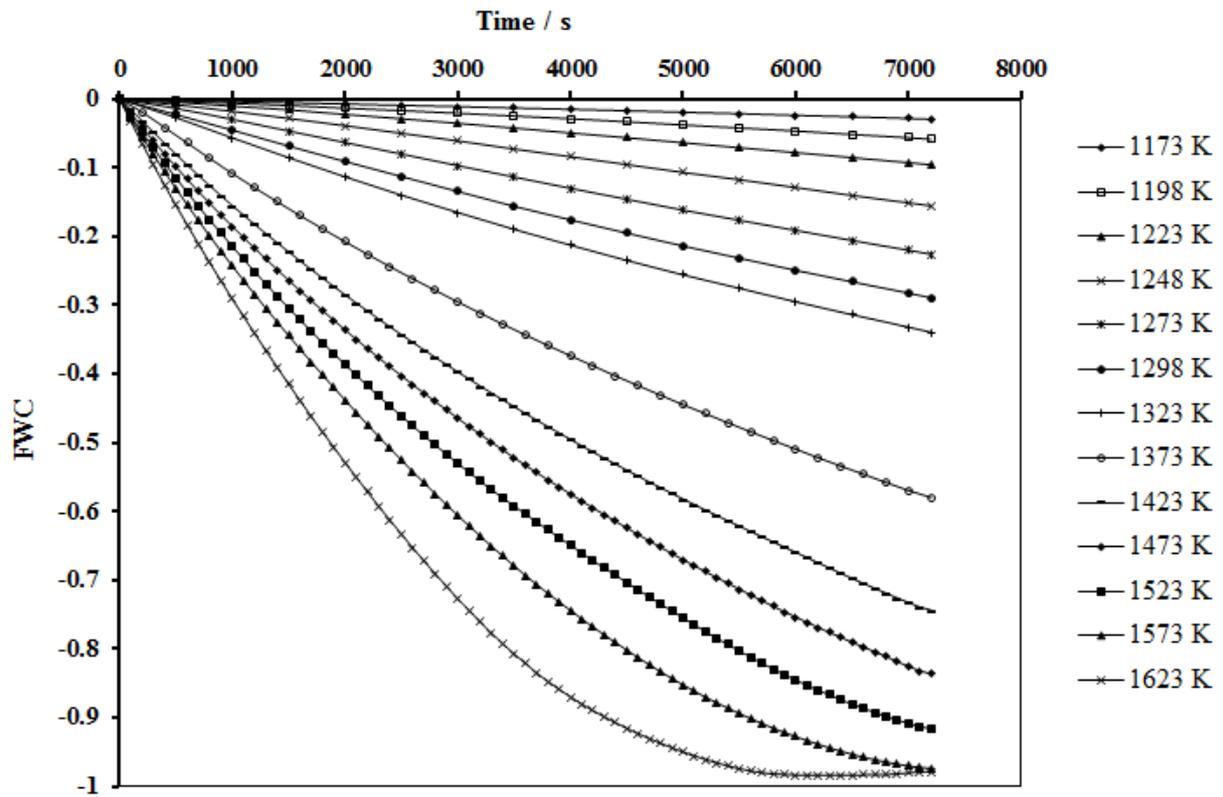


Figure 4. FWC data with time at various temperatures.

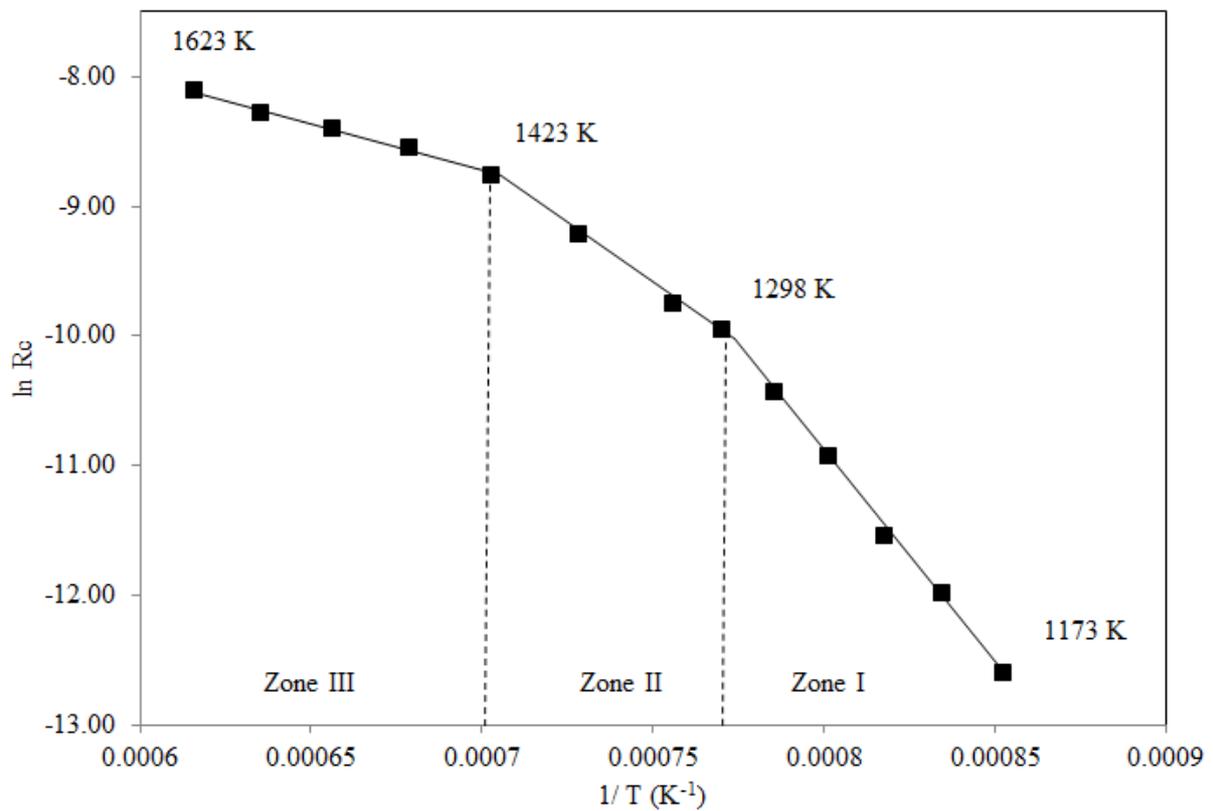


Figure 5. Arrhenius plot of $\ln R_C$ against $1/T$ for the coke analogue.

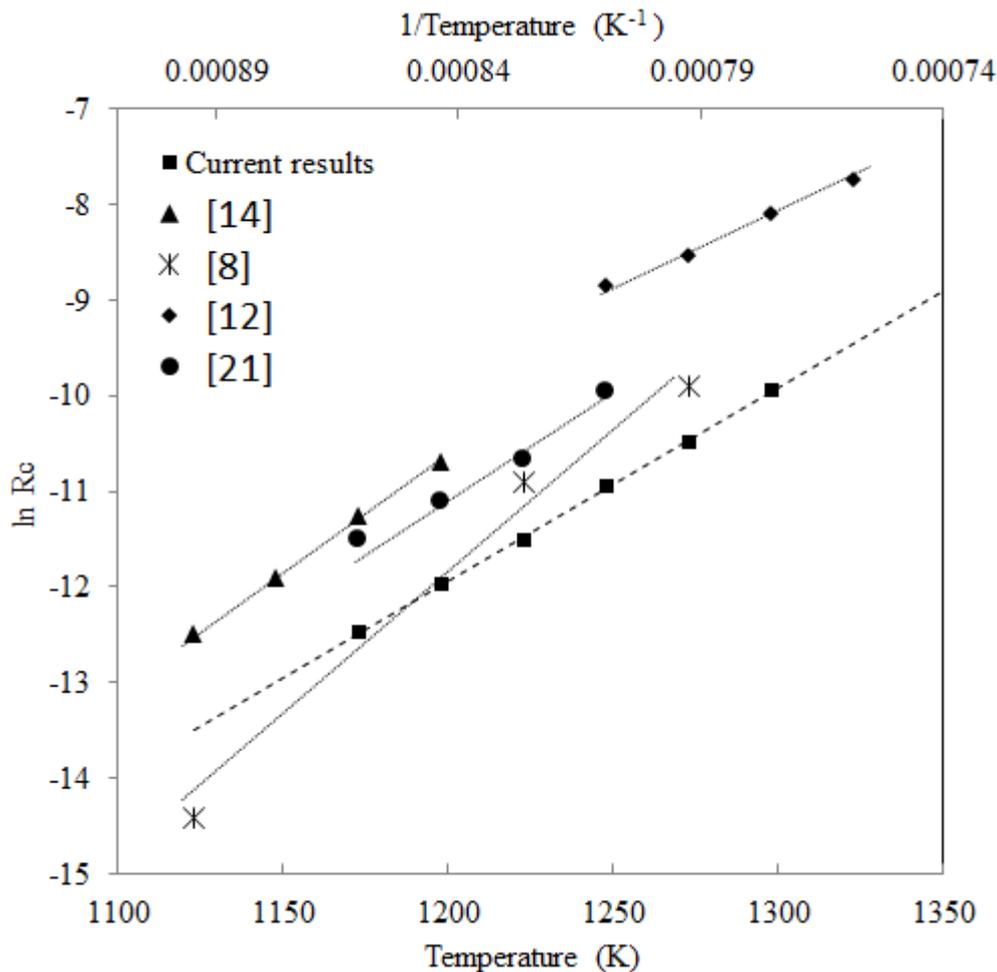


Figure 6. Comparison of the coke analogue reactivity in zone I with that of industrial coke.[8,12, 14,21]

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