KINETICS OF CATALYZED CO_2 COAL GASIFICATION REACTIONS

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Introduction

Sasol leads the world in the conversion of coal to oil and gas. This process is based on the gasification of **coarse** low grade coal in fixed bed Lurgi gasifiers. The majority of published research on gasification kinetics of coal however focus on the gasification reactions of **fine** coal particles. The aim of this paper is to (i) investigate the possibilities to enhance the reactivities of coals currently fed to our Lurgi gasifiers and (ii) get a basis for simulating the gasifiers by modeling the gasification reaction mechanism in order to obtain the microscopic rate-constants.

Experimental

High ash (> 20%) bituminous coals from two Sasol mines (Bosjesspruit and Sigma) were screened into a 4.75 by 6.7 mm fraction. A coal sample was mixed with an aqueous stream rich in calcium and sodium cations after which the excess water was evaporated. These cations are the dominant species responsible for the catalytic activity. Prior to reactivity measurements in a fixed bed reactor (FBR) the coal particles were pyrolyzed for two hours at 1173 K. The resulting char sample was heated in N_2 at 10 K min^{-1} to 1173 K at which point the nitrogen was replaced by CO_2. The weight loss as a function of reaction time was monitored, and this data was used to calculate the reactivity (r) at 50% carbon conversion according to a method described by Meijer *et al*[1]. The product gases were analyzed with a mass spectrometer.

Results and discussion

The CO_2 reactivities at 50% carbon conversion as well as the total cation concentration on the coals before and after treatment with the aqueous stream are listed in Table 1. According to these results mainly Na and Ca are loaded onto the coals. An increase in Na concentration from 0.22 to 3.2 % and Ca from 2.67 to 4.71 % results in ≈ 230% increase in reactivity for the two coals, and can mainly be attributed to the catalytic effect of the Na and Ca cations on the gasification reaction. The significant increase in reactivity is somewhat surprising for the high ash coals (~22% for Bosjesspruit and ~32 % for Sigma) used in this study and it will be discussed in more detail below.

Table 1 *Reactivities at 50% carbon conversion for treated and untreated Sasol coal samples*

	Bosjesspruit		Bosjesspruit with cations		Sigma		Sigma with cations	
Element	% cation	r (h^{-1})	% cation	r (h^{-1})	% cation	r (h^{-1})	% cation	r (h^{-1})
K	0.13		0.39		0.04		0.30	
Na	0.22		3.2		0.09		3.1	
Ca	2.67		4.71		0.92		2.96	
Mg	0.65	0.14	0.71	0.35	0.21	0.28	0.27	0.64

Gasification rate profiles have also been constructed from the reactivity versus carbon conversion data (Figure 1).

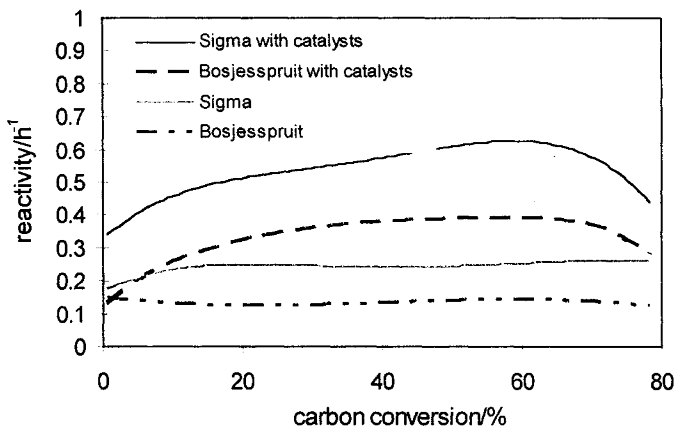

Figure 1 *Carbon conversion profiles for the reaction of Sasol coals with CO_2.*

The following information can be deduced from Figure 1: (i) The gasification rate profile is affected by the alkali and alkaline earth metals. In the non-catalytic gasification reactions, the rate does not change significantly with conversion. In the catalytic gasification reactions, the rate steadily increases with conversion, and it decreases at higher carbon conversion levels. (ii) The shape of the curves can be interpreted in terms of the "grainy pellet model"[1]. According to this model, the increase in reactivity with increasing carbon conversion in the case of the catalyzed reactions is due to an increase in the metal cation concentration at the external surface of small non-porous grains (particle constituents). (iii) At higher carbon conversion (~ 60 %) the decrease in the gasification rate can be attributed to a collapse of the particle structure, pore plugging, cation loss due to migration of Na into the pores[2] or Ca sintering[2] or reaction of the alkali metals with the mineral matter.

Gas analysis was performed in order to obtain experimental data to model the gasification reaction mechanism and determine the influence of increased metal cation loading on gas evolution. The gasification mechanism for catalyzed and uncatalyzed coal gasification reactions[1], outlined in Scheme 1, was modeled by using the experimental kinetic data (CO partial pressure versus time) in a modeling package (ZITA).

$$CO_2 + * \rightleftharpoons CO + O\text{-}* \qquad (1)$$

$$O\text{-}* + C_f \rightleftharpoons C(O) + * \qquad (2)$$

$$CO_2 + C_f \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C(O) + CO \qquad (3)$$

$$C(O) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO + C_f \qquad (4)$$

Scheme 1 General reaction mechanism for catalyzed CO_2 gasification of carbon.

Steps (3) + (4) in Scheme 1 are valid for uncatalyzed gasification. Step (3) represents the steps ((1) + (2)) in the catalyzed gasification reaction mechanism preceding the actual gasification reaction step, (4). * Represents a catalytically active site of unknown nature and O-* an oxygen containing alkali species involved in the oxygen transfer to a free carbon site C_f, resulting in the formation of the oxygen complex, C(O).

The total production of CO was calculated by integrating the rate of gas production over time, using the trapezoidal rule. These calculations showed that under the chosen experimental conditions, high alkali metal loading favour the formation of CO. This observation and the catalytic effect of the cations can be explained in terms of the gasification mechanism (Scheme 1).

In the case of steam gasification reactions, Veraa and Bell[3] argued that the primary function of the catalyst is to accelerate the rate-determining decomposition reaction step. The authors stated that if the activation energy is higher for this reaction step than for the complex-formation reaction step, an increase in cation loading would increase the CO concentration. Similar arguments can be true for CO_2 gasification reactions. To investigate this matter further the microscopic rate-constants in equations (3) and (4) were determined by modeling of the gasification mechanism outlined in Scheme 1, as described earlier on. Excellent agreement between modeled and experimental curves for pCO was obtained and confirms the validity of the modeling approach. The rate-constants calculated in this fashion are summarized in Table 2. It is clear from Table 2 that the major influence of the alkali metals are to accelerate the decomposition of the carbon-oxygen complex to produce CO.

Table 2. *Microscopic rate-constants (see Scheme 1) for the reaction of Sasol coals with CO_2.*

Sample	k_2 (atm^{-1} min^{-1})	k_{-2} (min^{-1})	k_1 (min^{-1})	k_{-1} (atm^{-1} min^{-1})
Bosjesspruit	1.14×10^{-3}	7.02×10^{-5}	9.97×10^{-2}	4.58×10^{-3}
Bosjesspruit with cations	3.39×10^{-4}	1×10^{-5}	9.01×10^{-1}	9×10^{-4}
Sigma	5.81×10^{-4}	5.64×10^{-4}	2.42×10^{-1}	9.55×10^{-4}
Sigma with cations	2.14×10^{-3}	8.82×10^{-4}	1.25	7.46×10^{-4}

Conclusions

The results in this study showed that alkali metal loadings onto high-ash South-African bituminous coals result in an increase in (i) the reactivity of the coals and (ii) the conversion of gasified carbon to CO. A unique contribution from this study is the modeling of the gasification mechanism for uncatalyzed and catalyzed CO_2 gasification of coarse coal particles to obtain microscopic rate-constants in the gasification mechanism. Future research will focus on (i) the kinetics and mechanism of the steam gasification catalyzed and uncatalyzed reactions of lump South-African coals (ii) modeling of the gasification mechanism for these reactions (iii) evaluation of the alkali metals in Lurgi gasifiers and (iv) use of the reaction and microscopic rate-constants in simulations of the gasification process.

References

1. R. Meijer, H.J. Mühlen, F. Kapteijn and J.A. Moulijn, *Fuel Processing Technology*, 28, 5, (1991)
2. M. Matsukata, E. Kikuchi and Y. Monta, *Fuel*, 1992, 71, 819.
3. M.J. Veraa and A.T. Bell, *Fuel*, 1978, 57.