

## Dual-Bed Gasification of Petcoke: Model Development and Validation

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In this work, the problem of modeling a previously proposed dual-bed gasification scheme [Sudiro et al., *Energy Fuels* 2008, 22, 3894–3901] is addressed. The process consists of a combustor and a gasifier, which are thermally coupled by the circulation of an inert solid, to use air instead of pure oxygen in the combustor. The coal gasification reactor is modeled, taking into account both chemical kinetics and mass transfer between gas phase and char particles. First, the model is developed and validated with reference literature and experimental data for conventional coal gasification using oxygen in both entrained-flow and fluid-bed gasifiers. A series of sensitivity analyses is performed with regard to a conventional gasifier fed by petcoke, and the effects of residence time and oxygen/carbon mass ratio in the feed are investigated over three process variables: char conversion at the gasifier exit, temperature at the gasifier exit, and amount of useful syngas (H<sub>2</sub> and CO) produced, in terms of N m<sup>3</sup> per ton of petcoke. Finally, the model is extended for application to the dual-bed process. Results from this simulation are compared to those obtained under equilibrium conditions, with an energetically equivalent syngas throughput.

### 1. Introduction

Coal is currently a major energy source, with regard to contributing to the world's energy systems, with a share of 23.80% of the worldwide energy production.<sup>2</sup> In fact, it provides 26% of the primary global energy needs and generates 41% of the world's electricity. The total global coal production, updated to 2007,<sup>3</sup> is 5543 million tonnes (5543 Mt) per year, which represents an increase of 6.5% over the previous year and a growth of 58.9% over the past 27 years. The top coal producer in the world is China, followed by the United States and then India.

The use of coal as a fuel is indeed a potential threat to the environment, because undesirable products that are generated during the combustion contaminate the atmosphere, water, and soil. To develop cleaner coal processes, and to obtain environmentally safer fuels, the liquefaction and gasification of coal have gained increased attention. In this respect, we would be required to ensure higher efficiencies and environmental acceptance, prolonging coal availability and proper replacement for oil and natural gas. This is only possible through a sustainable development of new coal conversion technologies, and one of these is gasification.

Coal gasification is currently performed with pure oxygen, because working with air has some disadvantages, such as the

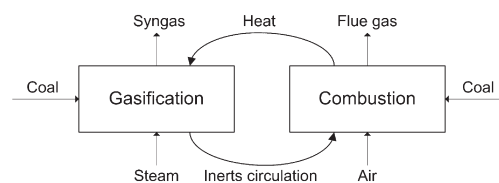


Figure 1. Conceptual scheme of a dual fluidized-bed (DFB) gasifier.

production of a lower gas quality, in terms of heating value,<sup>4</sup> which is due to the dilution of syngas with nitrogen. With oxygen, a higher-quality syngas can be obtained, but additional and relevant costs for oxygen production are required. As we have shown elsewhere,<sup>1</sup> a similar high-quality gas can be achieved using a dual fluidized-bed (DFB) system with steam as a gasification agent, and replacing the expensive high-purity oxygen with air to provide the gasification energy by combustion.

The basic idea of the DFB concept is to conduct the process in two separate fluidized-bed reactors: a gasification reactor and a combustor. In this way, the energy required by the endothermal gasification reactions is supplied by the separate combustion of coal, and of unreacted residual char from the gasification section, in a combustion reactor. The energy released during combustion is transported to the gasification reactor, along with the circulating bed material, thus making the DFB gasifier a self-sustained process. In summary, the DFB gasification system is able to physically separate the gasification and the combustion reactions, to gain a largely nitrogen-free product gas (see Figure 1).

This process scheme was developed in a previous work, where reactions were simulated at equilibrium.<sup>1</sup> In the present work, we intend to take into account both chemical kinetics and mass transfer. First, the model is developed and applied to a conventional coal gasification reactor for validation, then the same model is extended to the conceptual dual-bed gasification process. Also, for the case of conventional gasification

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**Table 1. Main Elemental Chemical Composition for Petcoke**

Proximate Analysis		Ultimate Analysis	
component	wt % mass (as received)	component	wt % mass (dry)
fixed carbon	80.6	C	89.23
volatile matter	9.6	H	3.59
water	9.3	O	0.10
ash	0.5	N	1.35
		S	5.22
		ash	0.50

with oxygen, the effects of the main process variables are investigated by some sensitivity studies, which report the influence of the oxygen/carbon mass ratio in the feed, and of the residence time, over the gasifier output, i.e., syngas outlet temperature, char conversion, and syngas molar productivity. Different from most literature publications, such as refs 5 and 6, where coal and/or petcoke gasification models are checked against available data, with respect to the syngas composition obtained, and to the process cold gas efficiency, one of the purposes of our paper is to correlate experimental data to a parameter that is important both for simulation and for reactor design: the value of the residence time of the gasifier.

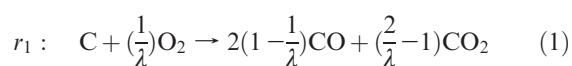
The model has been developed using the process simulator Aspen Plus, where kinetics and mass transfer have been added into the process as user subroutines.

## 2. Process Model

**2.1. Chemical System.** The following species were included in the model: O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub>, char (as graphite C), S (solid), H<sub>2</sub>S, and NH<sub>3</sub>. User-specified non-conventional solids have been defined to represent coal and ash. Suspended coal was assumed as char (as carbon graphite C).

Different types of coal, with a fixed composition, were used in the model development. For example, we refer to petcoke, which has the composition reported in Table 1,<sup>7</sup> to simulate a conventional gasifier base case from which a series of sensitivity analyses was conducted; also, the model was verified with two types of coal (Illinois coal #6 and Illinois coal #5; see section 3, “Simulation and Validation of Entrained-Flow Coal Gasifiers”, for details).

Four heterogeneous and three homogeneous reactions have been considered, as reported below (data are taken from refs 7 and 8). For the heterogeneous reactions, the rate expressions include both chemical kinetics and mass-transfer phenomena between the gas phase and char particles. For the homogeneous reactions, the rate expressions are reported below.



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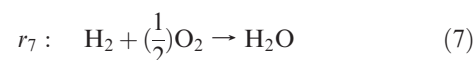
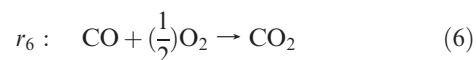
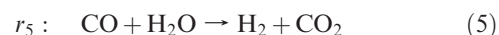
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**Table 2. Kinetic Parameters for Heterogeneous and Homogeneous Reactions**

reaction	$k_0$ (m/(s K <sup>B</sup> ))	$k_0$ (m <sup>3</sup> /(kmol s K <sup>B</sup> ))	$E_a$ (kJ/kmol)	B
$r_1^a$	1.220		$85.60 \times 10^3$	1
$r_2^a$	3.419		$129.70 \times 10^3$	1
$r_3^a$	208		$240.00 \times 10^3$	1
$r_4^a$	2083		$230.27 \times 10^3$	0
$r_5^a$		$2.96 \times 10^{-4}$	$40.7 \times 10^3$	2
$r_6^b$		$3.09 \times 10^8$	$99.8 \times 10^3$	0
$r_7^b$		$8.83 \times 10^8$	$99.8 \times 10^3$	0

<sup>a</sup>Data taken from Nagpal et al.<sup>7</sup> <sup>b</sup>Data taken from Weimer and Clough.<sup>8</sup>



The term  $\lambda$  in reaction 1 is related to the formation of CO versus CO<sub>2</sub>, which is calculated through the following relationship:

$$\text{CO}/\text{CO}_2 = A \exp\left(-\frac{E_a}{RT}\right) = 2\left(\frac{\lambda - 1}{2 - \lambda}\right) \quad (8)$$

where values of  $A = 10^{3.5}$  and  $E_a = 65$  kJ/mol are reported for high-pressure gasification.<sup>9</sup> For all reactions, heterogeneous and homogeneous, the kinetic constant  $k_j$  is dependent on the temperature (in Kelvin), in accordance with the Arrhenius law expression,

$$k_j = k_{j,0} T^B \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

and the parameters used are reported in Table 2.

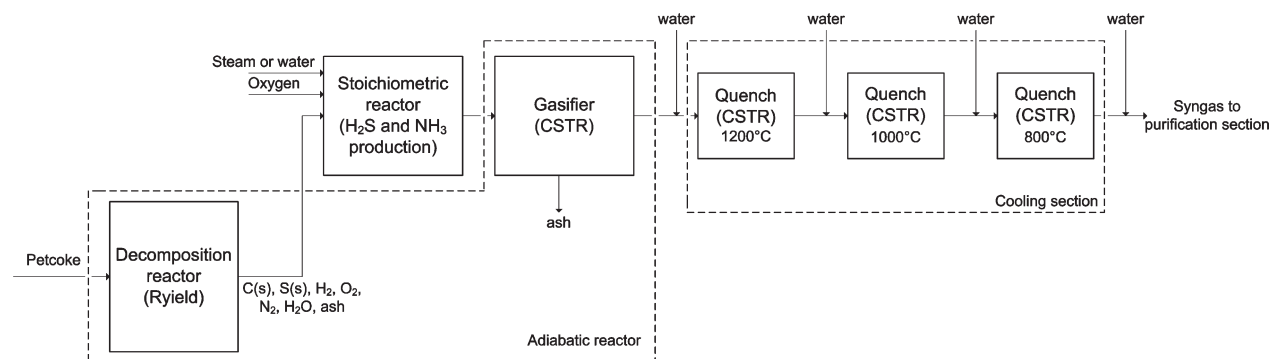
For the heterogeneous reactions, the rate expressions consider both chemical kinetics and mass-transfer phenomena between the gas phase and the char particles, under the hypothesis that reactions occur on the surface of the particles only, thus neglecting the contribution within the pores; according to ref 10, the relationship can be described as follows:

$$r_j = \frac{A_c c_{i,\text{bulk}}}{\left(\frac{1}{h_{M,i}} + \frac{1}{k_j}\right)} \quad (10)$$

where  $r_j$  is the reaction rate (expressed in units of kmol/(m<sup>3</sup> s)),  $c_{i,\text{bulk}}$  the average reacting gas concentration in the bulk (expressed in units of kmol/m<sup>3</sup>),  $k_j$  the kinetic constant (see eq 9), and  $h_{M,i}$  the mass-transfer coefficient for gas component  $i$  between the solid and gas phases (given in units of m/s) (see eq 12).  $A_c$  is the specific char surface area per unit reactor volume (expressed in units of m<sup>-1</sup>) and can be

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**Figure 2.** Block flow diagram of a conventional gasifier consisting of a gasification unit and a quench section.

defined as

$$A_c = \left(\frac{6}{d_p}\right)' y'_{\text{char}} \quad (11)$$

where  $d_p$  is the particle diameter (given in meters) and  $y'_{\text{char}}$  is the char volumetric fraction (that is, the volume filled by the char, with respect to the available reactor volume). In agreement with ref 7, we have assumed that the char particles are all spherical.

$$h_{M,i} = \frac{D_{i,\text{mix}}}{d_p} (2 + 1.1 Sc^{1/3} Re_M^{0.6}) \quad (12)$$

where  $D_{i,\text{mix}}$  is the diffusion coefficient of component  $i$  in the mixture, and  $Sc$  and  $Re_M$  (from ref 11) are the Schmidt and Reynolds numbers, respectively. Calculation of the gas-phase properties proceeds according to ref 12.

All char particles are assumed of the same spherical dimensions, so that, starting from a given particle diameter as input, the diameter reduction is uniform, according to ref 7. The particle diameter ( $d_p$ ) is dependent on char conversion ( $X_{\text{char}}$ ), according to

$$\left(\frac{d_p}{d_{p,0}}\right)^3 = 1 - X_{\text{char}} \quad (13)$$

where  $d_{p,0}$  is the initial particle diameter.

For the three homogeneous reactions, in eq 14, the rate of reaction  $r_5$  (water-gas shift, WGS) is reported, where  $K_{\text{WGS}}$  is the WGS equilibrium constant, which is calculated according to ref 13 (with the temperature  $T$  being expressed in Kelvin),

$$r_{\text{WGS}} = k_{\text{WGS}} \left( c_{\text{CO}} c_{\text{H}_2\text{O}} - \frac{c_{\text{CO}_2} c_{\text{H}_2}}{K_{\text{WGS}}} \right) \quad (14)$$

$$\ln K_{\text{WGS}} = -4.33 + \frac{4577.8}{T} \quad (15)$$

and eqs 16 and 17 show the reaction rates for reactions 6 ( $r_6$ )

and 7 ( $r_7$ ) (from refs 8 and 14, respectively):

$$r_6 = k_6 c_{\text{CO}} c_{\text{O}_2} \quad (16)$$

$$r_7 = k_7 c_{\text{H}_2}^2 \left( \frac{c_{\text{O}_2}}{c_{\text{CO}}} \right) \quad (17)$$

The chemical kinetics and mass transfer relations have been implemented in a Fortran routine, which is recalled by the source program of the process simulator that we have used (Aspen Plus<sup>TM</sup>). The Peng–Robinson equation of state with Boston–Mathias alpha function was applied as the thermodynamic model.

**2.2. Reactor Model.** A scheme of a first system to be modeled is shown in Figure 2, where the block flow diagram of a conventional gasifier, consisting of a gasification unit, followed by a quench section with water injection, is reported. CSTR behavior was assumed in all reacting units.

The model has first been developed for simulating a conventional entrained-flow gasifier using petcoke, steam, and oxygen as feedstocks. In typical entrained-flow gasifiers, high oxygen-to-carbon feed rates are used to obtain high temperatures (1200–1600 °C) and ensure high carbon conversion, and a syngas free of tars and phenols.<sup>15</sup> Coal and other solid fuel particles cocurrently react with steam and oxygen; coal can be fed either dry (commonly using nitrogen as the transport gas) or wet (carried in a water slurry) into the gasifier, which works at pressures in the range of 20–80 bar.<sup>15</sup> Because operating temperatures are very high, the reactions are quite fast and the residence time is in the range of 0.5–5 s.<sup>6</sup>

The gasification reactor is modeled in Aspen Plus<sup>TM</sup> using two units (see Figure 2): a RYield reactor and a CSTR reactor that are thermally coupled to obtain an adiabatic system. In the first unit, coal is broken into  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{S}(\text{solid})$ ,  $\text{C}(\text{solid})$ , and  $\text{H}_2\text{O}$  (moisture in the coal), whereas in the second one, reactions 1–7 occur. The kinetics of formation of  $\text{H}_2\text{S}$  and  $\text{NH}_3$  were not considered, and a stoichiometric reactor has been used to convert all the coal sulfur to  $\text{H}_2\text{S}$  and (empirically) 10%–50% of coal nitrogen to  $\text{NH}_3$ , with the balance of nitrogen remaining in the syngas produced, in the form of  $\text{N}_2$ .

In the absence of information on gasifier geometry, heat losses from a gasifier are taken into account by assuming their values to consist of 0.5% of the coal heat value for a refractory-lined gasifier, and 2% of the coal heat value for a gasifier where the shell is thermally protected by steam-

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generating coils. Such values are hypothetical, and, in a further design step, may be improved through better appraisal of heat losses, based on knowledge of the actual temperature, geometry, and materials used.

Raw gas exiting the gasifier usually requires significant cooling before the cleaning section, to avoid the reaction progress as well as damage to the downstream equipment. There are two main methods of cooling the gas: either using a high-temperature syngas cooler or by quenching the gases with water.<sup>6</sup> In the first case, the sensible heat in the gas leaving the gasifier is used to produce high-pressure steam and increase the efficiency of the process at the expense of higher investment cost. In the second case, the hot gas is quenched by evaporating water into the gas; during the quench phase, the water-gas shift is the only reaction that may occur significantly, leading to a substantial change in hydrogen and carbon monoxide composition.

In our simulation, a direct quench was assumed, where the syngas comes into contact with a stream of liquid water that evaporates. This section has been simulated with three adiabatic continuously stirred tank reactors (CSTR) in series, operating at different temperatures: 1200, 1000, and 800 °C, respectively. These temperatures are obtained by varying the amount of water added to the syngas stream. After the third reactor, there is another addition of liquid water, to cool the syngas to saturation (200–300 °C); the water mass flow rate is adjusted to saturate the gas with steam, with no further water-gas shift reaction occurring.

### 3. Simulation and Validation of Entrained-Flow Coal Gasifiers

The results obtained for conventional gasification have been compared with literature and experimental data to validate the model (see refs 16 and 17).

Operating data for an entrained-flow coal gasifier have been reported by Shelton and Lyons,<sup>16</sup> using Illinois #6 coal as the feedstock. This report was used for validation of the model described in section 2, “Process Model”. Table 3 gives the proximate and ultimate analyses of the coal used and the operating conditions of the plant. Table 4 shows a comparison of the model simulation results with the plant operating data from the report.<sup>16</sup> The simulated values for the exit gas composition after the quench and the gasification performance indexes are seen to be in good agreement with data. The residence time for the gasification reactor is set to 3 s: we have taken this value to obtain an acceptable carbon conversion (>99%). In the quench section, for each one of the three notional reactors described above, a total time of reaction of 0.15 s was used to account for the path to be covered by the syngas before fully reaching the water zone.

The choice of a precise value for the residence time in the gasifier can be explained by Figure 3, which shows the trend of char conversion simulated for different residence time values. It is clear that, when the residence time is higher than 3 s, the difference in the char conversion is very low, and its value is >99.5%. In addition, the difference between char conversion

**Table 3. Coal Composition and Operating Conditions (Data Taken from ref 16) Used for Simulating a Conventional Entrained-Flow Gasifier**

parameter	value
Coal Properties: Proximate Analysis	
fixed carbon	44.19 wt %
volatile matter	34.99 wt %
ash	9.70 wt %
moisture	11.12 wt %
Coal Properties: Ultimate Analysis	
component	
C	71.72 wt % (dry)
H	5.06 wt % (dry)
N	1.41 wt % (dry)
O	7.75 wt % (dry)
S	3.15 wt % (dry)
ash	10.91 wt % (dry)
high heating value, HHV <sup>a</sup>	27135 kJ/kg
Operating Conditions	
pressure	42 bar
O <sub>2</sub> /C (by weight)	1.23
water content in the feed <sup>b</sup>	33.5 wt %
gasifier residence time	3 s
quench residence time <sup>c</sup>	0.05 s
wet coal	127744 kg/h
O <sub>2</sub> (95% molar purity)	105088 kg/h
water	42991 kg/h

<sup>a</sup> Data taken from Shelton and Lyons.<sup>16</sup> <sup>b</sup> Coal is mixed with water to produce a slurry that is 33.5 wt % water, and this value includes both the added water and the moisture contained in the coal. <sup>c</sup> Here, a residence time of 0.05 s is assumed for each CSTR unit, for a total quench residence time of 0.15 s.

obtained at 3 and 5 s is only 0.28%; in fact, at 3 s, char conversion is 99.46%, while at 5 s, char conversion is 99.74%, so that the small conversion increase with residence time does not justify a larger reactor volume, which would involve significantly higher capital costs. This point explains the choice done for the residence time in the gasifier.

A second validation was performed with gasification data taken from ref 17 for an entrained-flow coal gasifier using Illinois No. 5 coal as feedstock. In this case, coal is fed dry, using nitrogen as the transport gas, and reacts with steam and oxygen. Results are compared at the exit of the gasification section, before entering the quench (only these data are available). Table 5 gives the coal composition used and the operating conditions of the plant. As in the previous example, the residence time for the gasification reactor was set to 3 s, to reproduce the experimental char conversion.

Simulation results are in fairly good agreement with the plant exit gas composition and the plant data, as shown in Table 6.

In summary, the present model was determined to allow a reasonably accurate simulation of an entrained-flow gasifier operation over a wide range of operating conditions. Discrepancies can be considered acceptable if proper account is taken of uncertainties or nondeclared parameters within published data, among which we may mention the actual geometry of gasifiers (and of downstream cooling or quenching apparatus), the oxidant feed temperature, and heat losses as major ones, and the initial coal size and the quench water temperature (when applicable) as minor ones.

We note that the model that we have used was also validated by Nagpal et al.<sup>7</sup> for moving-bed reactors. In the work of Nagpal et al.,<sup>7</sup> model simulation results were compared with plant operating data for different types of coal.

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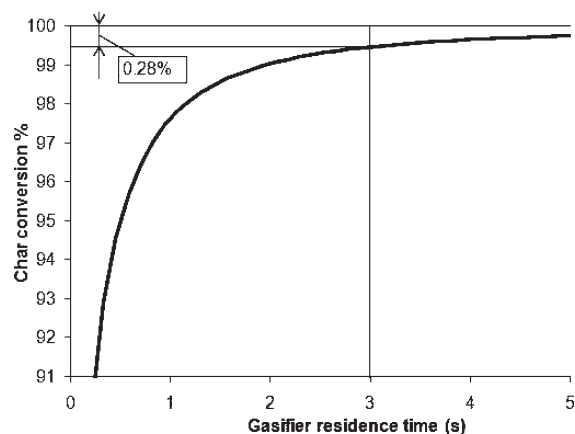
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**Table 4. Comparison between the Model Simulation Results and Literature Data**

parameter	plant operating data <sup>a</sup>	simulation results
product gas composition		
N <sub>2</sub>	1.94 mol % (dry)	1.84 mol % (dry)
H <sub>2</sub>	37.61 mol % (dry)	36.23 mol % (dry)
CO	49.83 mol % (dry)	49.24 mol % (dry)
CO <sub>2</sub>	10.54 mol % (dry)	12.63 mol % (dry)
CH <sub>4</sub>	0.08 mol % (dry)	0.05 mol % (dry)
H <sub>2</sub> /CO <sup>b</sup>	0.75	0.74
T out, gasifier	1371 °C	1363 °C
T out, quench	218 °C	222 °C
cold gas efficiency (based on HHV)	c	76.38%
cold gas efficiency after quench section (based on HHV)	74.95%	71.42%
char conversion	d	99.46%

<sup>a</sup> Data taken from Shelton and Lyons.<sup>16</sup> <sup>b</sup> Value calculated after quench section. <sup>c</sup> Not reported by the DOE. It is not possible to calculate it from the composition and flow rate of syngas, because only the values at the exit of the quench section are reported. <sup>d</sup> Not reported by the DOE.



**Figure 3.** Char conversion as a function of the residence time in the entrained flow gasifier for a simulation with data taken from ref 16.

The simulated values for the exit gas composition and temperature were determined to be in good agreement with plant data.

Therefore, the application of the kinetic model also to fluid-bed reactors is believed to be justified, because of the residence times (10–100 s), which are intermediate between those typical of entrained flow gasifiers (< 5 s), and those relevant to moving-bed gasifiers (15–60 min).<sup>6</sup> For a better assurance of applicability to our case, the model that we have developed was also validated on data for a fluid-bed reactor, as reported by Higman and Van Der Burgt.<sup>6</sup> These authors provide data for a fluid-bed gasifier, operating at 30 bar with bituminous coal, an O<sub>2</sub>/C ratio of 0.81 (weight basis), and a steam to carbon (H<sub>2</sub>O(g)/C) ratio of 0.56 (weight basis). Table 7 shows the comparison between these data and our simulation results: it is possible to see that a reasonable performance of the model is ensured, with the main discrepancies essentially associated with the extent of the CO shift reaction.

#### 4. Sensitivity Studies

After validating the model that was developed, a series of sensitivity analyses was performed, with respect to a base case, with a petcoke feed of 100 t/h. The effects of residence time and O<sub>2</sub>/C mass ratio in the feed were investigated, with respect to the following three process variables:

- (1) char conversion at the exit of the gasifier,
- (2) temperature of the gasifier, and
- (3) amount of syngas produced (N m<sup>3</sup> of H<sub>2</sub> and CO per ton of maf petcoke fed).

**Table 5. Coal Composition and Operating Conditions (Data Taken from ref 17) Used To Simulate a Conventional Entrained-Flow Gasifier**

parameter	value
Coal Properties: Proximate Analysis	
ash	9.5 wt %
moisture	2.3 wt %
Coal Properties: Ultimate Analysis	
component	
C	69.3 wt % (dry)
H	4.9 wt % (dry)
N	1.6 wt % (dry)
O	9.2 wt % (dry)
S	3.7 wt % (dry)
ash	11.3 wt % (dry)
high heating value, HHV <sup>a</sup>	27340 kJ/kg
Operating Conditions	
pressure (bar)	24 bar
O <sub>2</sub> /C (by weight)	1.14
steam/C (by weight)	0.07
residence time (s)	3 s
wet coal	9083 kg/h
O <sub>2</sub>	7000 kg/h
steam	445.8 kg/h
N <sub>2</sub>	700.0 kg/h

<sup>a</sup> Data taken from the following website: <http://www.ecn.nl/phyllis>.

Sensitivities were performed by varying the O<sub>2</sub>/C mass ratio in the feed in the range of 0.9–1.2, for three different residence time values (2, 2.5, and 3 s), and the results also were compared with those calculated at equilibrium. As the base case, a conventional entrained-flow gasifier was simulated, with an O<sub>2</sub>/C ratio equal to 1.13 (weight basis), a H<sub>2</sub>O(g)/C ratio equal to 0.40 (weight basis), and a residence time of 3 s. Under these conditions, a char conversion of 98.9% is obtained, the outlet temperature of the gasifier is 1389 °C, and 9563 kmol/h of dry syngas are generated from 100 t/h of petcoke, corresponding to 2387 N m<sup>3</sup> (CO + H<sub>2</sub>) per ton of petcoke (maf), in agreement with the literature data; for entrained-flow gasifiers, this value is in the range of 2000–2300, depending on the coal used.<sup>6</sup> Also, the lower heating value (LHV) in the syngas is ~11.7 MJ/N m<sup>3</sup>, in accordance with the literature data.<sup>6</sup>

Figures 4 and 5 show the sensitivities of the gasifier output temperature and char conversion, respectively, on the O<sub>2</sub>/C mass ratio: in both cases, four curves are reported, corresponding to three residence time values and the result obtained at equilibrium. It is clear that, for a given residence time, a higher oxygen value in the feed increases the temperature

**Table 6. Comparison between the Model Simulation Results and Literature Data**

	plant operating data <sup>a</sup>	simulation results
product gas composition		
N <sub>2</sub>	4.58 mol % (dry)	4.00 mol % (dry)
H <sub>2</sub>	29.02 mol % (dry)	27.66 mol % (dry)
CO	63.65 mol % (dry)	65.34 mol % (dry)
CO <sub>2</sub>	1.63 mol % (dry)	0.82 mol % (dry)
CH <sub>4</sub>	0.20 mol % (dry)	0.81 mol % (dry)
H <sub>2</sub> S	0.92 mol % (dry)	1.36 mol % (dry)
H <sub>2</sub> /CO	0.46 mol	0.42 mol
T out, gasifier	1527 °C	1533 °C
cold gas efficiency (based on HHV)	81.40%	83.72%
char conversion	99.70%	98.23%

<sup>a</sup> Data taken from Ni and Williams.<sup>17</sup>**Table 7. Comparison between the Model Simulation Results and Literature Data for a Fluid-Bed Gasifier**

	plant operating data <sup>a</sup>	simulation results
product gas composition		
N <sub>2</sub>	1.6 mol % (dry)	1.7 mol % (dry)
H <sub>2</sub>	37.3 mol % (dry)	39.1 mol % (dry)
CO	52.0 mol % (dry)	48.3 mol % (dry)
CO <sub>2</sub>	5.3 mol % (dry)	7.5 mol % (dry)
CH <sub>4</sub>	3.5 mol % (dry)	3.1 mol % (dry)
H <sub>2</sub> S	0.3 mol % (dry)	0.3 mol % (dry)
T out, gasifier	1000 °C	971 °C

<sup>a</sup> Data taken from Higman and Van Der Burgt.<sup>6</sup>

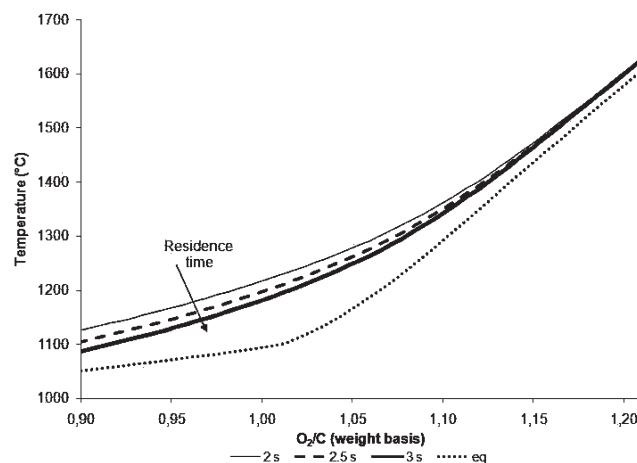
and, consequently, the char conversion. The temperature increase is due to the combustion reactions: with an O<sub>2</sub>/C ratio of > 1.15, the temperature is close to that obtained under equilibrium conditions. Instead, for a given mass flow rate of oxygen, a higher residence time decreases the temperature, because of the fact that gasification reactions are highly endothermic; the char conversion increases accordingly.

Figure 6 shows the amount of (CO + H<sub>2</sub>, in units of N m<sup>3</sup>) produced per ton of maf petcoke, as a function of the O<sub>2</sub>/C mass ratio (again, four curves are shown: three residence times and one at equilibrium). For a given residence time value, if the amount of oxygen in the feed increases, the observed variable first increases and then reaches a maximum and decreases. The figure does not show the range where feed oxygen, and the temperatures attained, are so low that the syngas production decreases to nil. The range to the right of the maximum corresponds to oxygen rates sufficiently high to cause the combustion of the produced syngas. It is also clear that, for higher residence time values, more syngas is produced; however, there will be an optimum point constrained by economical considerations between the residence time (or reactor volume) and syngas productivity.

Finally, the value of the H<sub>2</sub>/CO molar ratio in the syngas also is dependent on the amount of oxygen used (not shown in the figure). For a fixed value of the residence time, with increasing oxygen in the feed, the H<sub>2</sub>/CO molar ratio decreases, because of the fact that the temperature increases, thus creating less-favorable conditions for the water-gas shift reaction. For a fixed value of the O<sub>2</sub>/C mass ratio, with increasing residence time, the H<sub>2</sub>/CO molar ratio in the syngas at the exit of the gasifier increases, because of the longer time that is required for the water-gas shift reaction to occur.

## 5. Dual-Bed Simulation Results

The model validated in the previous section was applied to simulate a DFB gasification process, which was previously examined under equilibrium conditions.<sup>1</sup> Figure 7 shows the

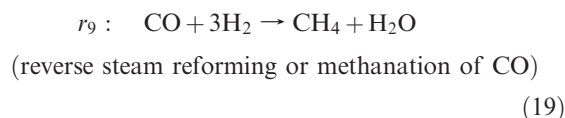
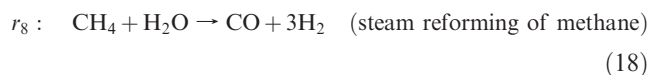


**Figure 4.** Gasifier output temperature, as a function of the O<sub>2</sub>/C mass ratio, for three different values of the residence time (eq is the curve obtained under equilibrium conditions).

block flow diagram of the dual-bed gasification process presently simulated; the main flow rates also are reported in the figure.

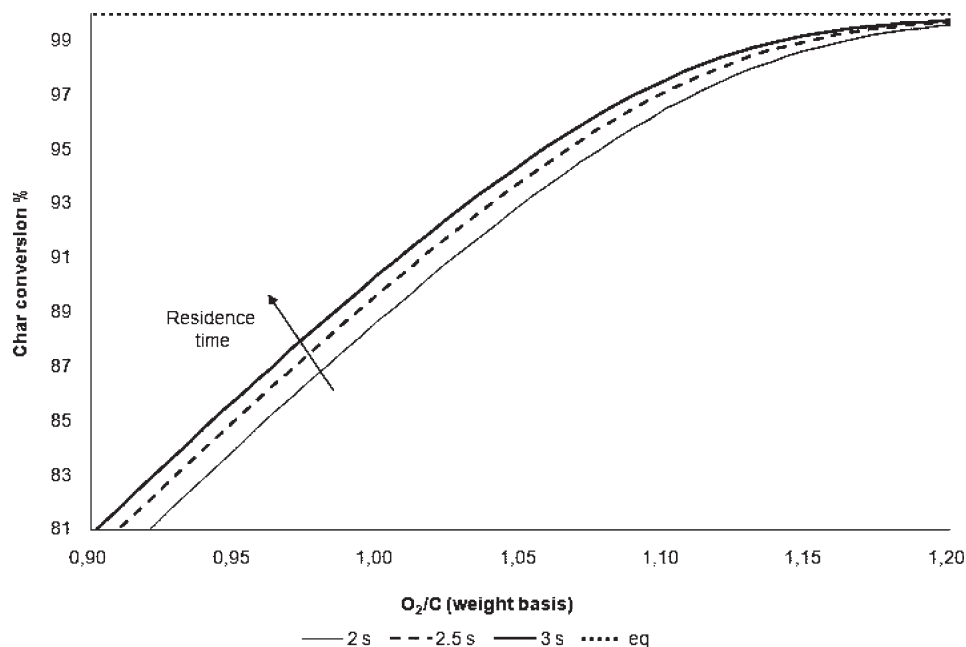
The scheme consists of two parts: the combustor and the gasifier, working at temperatures of 990 and 860 °C, respectively.

Note that temperatures in a fluidized bed should be kept at < 1000 °C, to avoid ash softening and agglomeration in coal processing.<sup>1</sup> Above this temperature the CH<sub>4</sub> steam reforming reaction is completely shifted to the production of CO and H<sub>2</sub>. However, at lower temperatures, the syngas produced is indeed heavier, and it is richer in methane, because this reaction cannot be considered as irreversible anymore. Therefore, two additional reaction rates equations have been included in the model (actually one reaction plus its reverse form):

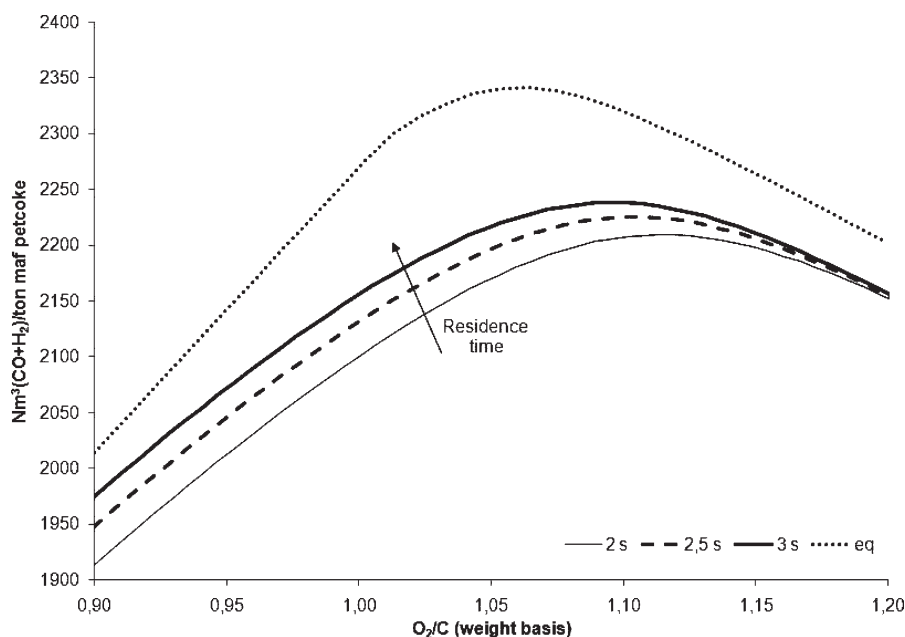


The kinetics of these reactions were taken from Dobrego et al.<sup>18</sup> Mass generation of component *i* due to reaction

(18) Dobrego, K. V.; Gnesidilov, N. N.; Lee, S. H.; Choi, H. K. Overall chemical kinetics model for partial oxidation of methane in inert porous media. *Chem. Eng. J.* **2008**, *144*, 79–87.



**Figure 5.** Gasifier output char conversion (expressed as a percentage), as a function of the  $O_2/C$  mass ratio, for three different values for the residence time (the dotted curve (denoted as “eq”) is the curve obtained under equilibrium conditions).



**Figure 6.** Amount of  $(CO + H_2)$ , in units of  $N m^3$ , produced per ton of maf petcoke, as a function of the  $O_2/C$  mass ratio, for three different residence time values (the dotted curve (denoted as “eq”) is the curve obtained under equilibrium conditions).

$r_8$  (expressed in units of  $kg/(m^3 s)$ ) was calculated in accordance with the kinetic expression given as eq 20:

$$r_i = v_i A \exp\left(-\frac{E}{T}\right) PM_i \left(\frac{P}{RT}\right)^2 w_{CH_4} w_{H_2O} \quad (\text{reaction } r_8) \quad (20)$$

where  $v_i$  is the stoichiometric coefficient for component  $i$  (negative for reagents and positive for products),  $A$  the pre-exponential factor of the rate constant ( $A = 2.5 \times 10^{23} m^3/(kmol s)$ ), and  $E$  the activation energy divided by the universal gas constant  $R$  ( $E = 59\,000 K$ );  $PM_i$  is the molecular weight (in units of  $kg/kmol$ ) of component  $i$  and  $w_i$  indicate mass fractions.  $P$  is the pressure (in Pascal),  $T$  the temperature (in Kelvin), and  $R$  the universal gas constant.

The reverse reaction rate expression was evaluated via the equilibrium constant, which was calculated from the standard Gibbs energy change of reaction  $\Delta G^0$  ( $\sum v_i \Delta G_i^0$ ), by the CHEMKIN correlations.<sup>19</sup> Accordingly, we found that the mass generation of component  $i$  due to reaction  $r_9$  (expressed in units of  $kg/(m^3 s)$ ) can be calculated by

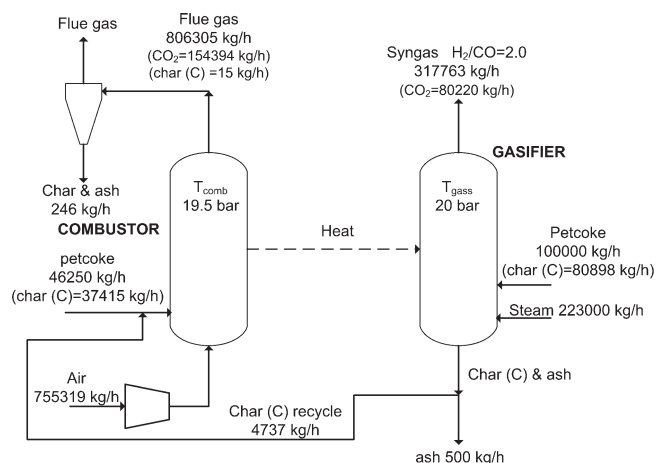
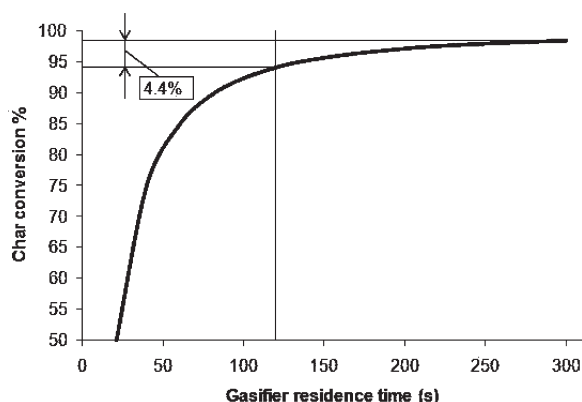
$$r_i = v_i A_{rev} \exp\left(-\frac{E_{rev}}{RT}\right) PM_i \left(\frac{P}{PM_{mix}}\right)^2 \left(\frac{P}{P_0}\right) y_{CO} y_{H_2}^3 \quad (\text{reaction } r_9) \quad (21)$$

(19) Frenklach, M.; Bowman, T.; Smith, G.; Gardiner, B. Available via the Internet at [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/).

**Table 8. Comparison between Syngas Obtained from Simulation of the Dual-Bed Gasifier under Equilibrium Conditions and Simulations Taking into Account Kinetics**

component	Kinetics		Equilibrium	
	(kmol/h)	molar fraction (% , dry)	(kmol/h)	molar fraction (% , dry)
H <sub>2</sub>	7922.2	54.8	7522.9	53.2
CO	3955.8	27.4	3817.0	27.0
CO <sub>2</sub>	1822.8	12.6	1879.2	13.3
CH <sub>4</sub>	562.4	3.9	727.8	5.2
H <sub>2</sub> O	5299.5	0.0	4176.8	0.0
N <sub>2</sub>	39.2	0.3	41.5	0.3
H <sub>2</sub> S	147.5	1.0	140.7	1.0
NH <sub>3</sub>	8.7	0.1	a	

<sup>a</sup> Under equilibrium conditions, we have not considered the formation of ammonia; however, all the nitrogen in the coal is transformed to N<sub>2</sub>.

**Figure 7.** Scheme, and main flow rates, of the dual-bed gasification simulated process.**Figure 8.** Char conversion as a function of the residence time in the fluid-bed gasifier for the dual-bed configuration.

where  $A_{rev} = 1.0827 \times 10^{-2} \text{ s}^3/(\text{kmol m})$  and  $E_{rev} = 250\,808 \text{ kJ/kmol}$ ;  $PM_{mix}$  is the molecular weight of the mixture and  $y_i$  represents the molar fraction of the component  $i$ .

The simulation of the dual bed with kinetics was performed under the assumption to achieve a syngas with the same energy content obtained in the case at equilibrium (968.5 MW, based on the LHV), and with the same H<sub>2</sub>/CO molar ratio (equal to 2). In addition, we decided to use a mass flow rate of petcoke sent to the gasification section that was equal to 100 t/h. Residence times of 60 and 120 s were assumed for the combustion and gasification reactors, respectively, in agreement with typical values for fluid-bed reactors, which are in the range of 10–100 s.<sup>6</sup> The choice of this precise value

**Table 9. Comparison between Gasification Performances Obtained from Simulation of the Dual-Bed Gasifier under Equilibrium Conditions and Simulations Taking into Account Kinetics**

	Dual-Bed Gasification	
	kinetics	equilibrium
H <sub>2</sub> /CO molar ratio	2.0	2.0
(H <sub>2</sub> + CO)/C <sub>TOTAL</sub>	1.2 (mol)	1.2 (mol)
CO <sub>2</sub> /H <sub>2</sub> + CO	0.45 (mol)	0.43 (mol)
char conversion at the gasifier	94.1%	100.0%
cold gas efficiency, based on LHV	83.4%	87.4%
duty required for gasification section	293.7 MW <sub>th</sub>	271.5 MW <sub>th</sub>
inerts circulation/C <sub>TOTAL</sub> (weight basis)	52.1	50.5
heat value of syngas, based on LHV	10.8 MJ/N m <sup>3</sup>	11.0 MJ/N m <sup>3</sup>

for the residence time in the fluid-bed gasifier can be explained by Figure 8, which shows the trend of char conversion as a function of the residence time. It is clear that, when the residence time is > 100–150 s, the difference in char conversion is negligible, and its value is > 95% for residence times of > 150 s. The difference between char conversion obtained at 120 and 300 s is 4.4%, which is an increase that hardly justifies a reactor volume that is 2.5 times larger, involving significantly higher capital costs. It would rather appear reasonable, on the other hand, to select a value of the residence time such that the unconverted char could provide, when recycled to the combustor, the heat required by the gasifier.

Results comparing the dual-bed process with and without kinetic limitations are summarized in Tables 8 (component flow rates) and 9 (process performance indexes) and are discussed below.

First of all, when accounting for the chemical kinetics, we note that not all of the carbon was converted to syngas, thus requiring a recycle to the combustor to consume it all. In contrast, under ideal equilibrium conditions, all the carbon could be assumed to react in the gasifier with complete conversion.<sup>1</sup> If the carbon conversion is not complete, the unconverted carbon may be recycled to the combustor together with circulating inerts, to substitute a part of the mass flow rate of fresh feed to combustion.

As expected, dual-bed simulation using the kinetic model resulted in a worse general performance, when compared to the equilibrium assumption, as the production of syngas with the same energy content requires a higher gasification heat (by ~8.2%). A larger thermal duty for the gasifier needs more petcoke to be fed to the combustion section. Also, because of the increased thermal power required by the gasifier with kinetics, a higher circulating mass ratio of inerts to char is needed (see Table 9). For the same reason, the cold gas efficiency is lower than that obtained at equilibrium (83.4% versus 87.4%).



Nevertheless, thanks to the effect of lower operating temperatures, which are typical of fluidized beds, the cold gas efficiency value remained higher than that achieved in conventional gasification with oxygen. According to Higman and Van Der Burgt,<sup>6</sup> this is expected to be in the range of 80%–84%. However, Guo et al.<sup>20</sup> reported the following cold gas efficiency values for entrained flow gasifiers: 81.4% for the Shell Coal Gasification Process (SCGP), 77.5% for Shell Koppers technology, and in the range of 71%–73% for the GSP gasification (technology by Siemens). According to Liu and Kojima,<sup>21</sup> entrained flow gasifiers have cold gas efficiencies in the range of 71%–74%. The Texaco technology, which is based on an entrained-flow gasifier, has a cold gas efficiency of ~80%, according to ref 6, which is the same value reported for fluidized-bed gasifiers (for example, the Kellogg–Rust–Westinghouse (KRW) gasifier).<sup>22</sup>

With regard to the LHV of the syngas produced, the values obtained with conventional gasifiers using oxygen are quite similar to that of the DFB system. For example, according to Shelton and Lyons,<sup>16</sup> the syngas after the quench has an LHV of ~10.0 MJ/Nm<sup>3</sup>, and given the data of Ni and Williams,<sup>17</sup> the energy content of the syngas is 11.7 MJ/Nm<sup>3</sup>, which is also consistent with data from ref 6, where the performance of a Lurgi process (MPG, Lurgi's Multipurpose Gasification Process) is reported (LHV ≈ 12 MJ/kg). The LHV value that we obtained at the outlet of the dual-bed system is 10.8 MJ/Nm<sup>3</sup>. In addition, with regard to conventional gasifiers, the dual-bed gasification scheme has the advantages of producing a nitrogen-free syngas, even if air is used as an oxidant, and avoiding the need for an expensive (both energetically and

economically) air separation unit (ASU) to supply high-purity oxygen.

## 6. Conclusions

The problem of simulating the performances of a dual-bed gasification scheme using air instead of pure oxygen in the combustor was addressed, by taking into account both chemical kinetics and mass transfer between the gas phase and char particles.

First, a model for entrained-bed gasification of petcoke was developed and validated using reported data for conventional coal gasification reactors. It was shown that the model developed allows a reasonably accurate simulation of gasification of feedstocks with widely different compositions, as demonstrated by comparison with experimental plant output gas compositions for both entrained-flow and fluid-bed gasifiers. It was possible to calculate the range for the residence time of an entrained-flow gasifier, which turned to be 2–3 s. Sensitivity studies showed the effects of residence time and O<sub>2</sub>/carbon mass ratio in the feed on three main variables of the process: char conversion and temperature at the exit of the gasifier, and the amount of syngas produced (expressed in units of Nm<sup>3</sup> of syngas (H<sub>2</sub> and CO) per ton of petcoke).

The model was then applied to a dual fluidized-bed (DFB) gasifier, to compare the results obtained with a simulation of the same system under equilibrium conditions.<sup>1</sup> When kinetics were taken into account, a general decrease in performance was observed; in particular, a higher heat input was required by the gasification section, involving a higher mass ratio between the circulating sand and the total feed. Finally, it was shown that the cold gas efficiency obtained with a simulation based on kinetics is noticeably lower (83.4%) than that obtained at equilibrium (87.4%); however, the value of this parameter remains slightly high, comparable to those typical of conventional gasification with oxygen, and a similar conclusion also holds for the LHV of the syngas produced.

If an overall energy balance were done encompassing, in the case of conventional gasification with pure oxygen, also the oxygen enrichment process itself, then the energy balance would probably revert in favor of the dual-bed gasification.

(20) Guo, X.; Dai, Z.; Gong, X.; Chen, X.; Liu, H.; Wang, F.; Yu, Z. Performance of an entrained-flow gasification technology of pulverized coal in pilot-scale plant. *Fuel Process. Technol.* **2007**, *88*, 451–459.

(21) Liu, H.; Kojima, T. Theoretical study of coal gasification in a 50 ton/day HYCOL entrained flow gasifier. I. Effects of coal properties and implications. *Energy Fuels* **2004**, *18*, 908–912.

(22) Akunuri, N. Modeling the Performance, Emissions, and Costs of Texaco Gasifier-Based Integrated Gasification Combined Cycle Systems. Available via the Internet at <http://www.scribd.com/doc/7141421/Modeling-the-Performance-Emissions-And-Costs-of-Texaco-Gasifier-based-Integrated-Gasification-Combined-Cycle-Systems>.