39   GASIFICATION OF CHAR PARTICLES WITH CO_2 AND H_2O

Michiel J. Groeneveld and W.P.M. van Swaaij

Department of Chemical Engineering
Twente University of Technology
P.O. Box 217, 7500 AE Enschede
Netherlands.

ABSTRACT

Gasification of large char particles with CO_2 and H_2O has been investigated both
experimentally and with model studies.
A local volumetric rate model is derived that takes into account the chemical reaction
rate and the effective diffusivity being a function of the local carbon conversion
and therefore a function of time and position within the particle.
The model includes shrinking unreacted core and homogeneous reaction as extreme cases.
Chemical reaction rates of powdered deal wood char were measured for different CO_2
and/or H_2O concentrations (0.05 - 2 mol/m^3) and as a function of the carbon conversion
and temperature (1073 - 1273 K) by means of a modified thermobalance.
In separate single particle tests the effective diffusivity has been determined for
different carbon conversions.
A specially designed single particle reactor has been used for local carbon conversion
measurement within 0,04 m particles. Carbon conversion profiles obtained differ from
those predicted by the shrinking core and homogeneous reaction extremes but could be
very well explained by the local volumetric rate model.
As an example results obtained from a 3 kg/h co-current moving bed wood gasifier are
presented.
Char conversion, particle diameter and temperature profiles agree well with the re-
duction zone model based on the local volumetric-rate particle model.

INTRODUCTION

Worldwide renewed interest is being given to gasification as a means of utilising solid
carbonaceous materials, such as coal and biomass, for the production of energy and
chemicals (e.g. Klass, 1978). Allthough gasification is a very old process, it is only
relatively recently that chemical reaction engineering work has been devoted to this
process. The reasons for this are the complex physical and chemical properties of the
solid fuel and the many reactions involved, which cannot be specified precisely for
reactor design. During gasification the solid fuel successively dries, pyrolysis in
which the solid residue develops a higher carbon content – and reacts with O_2, H_2O,
CO_2 and H_2. These latter heterogeneous char – gas reactions control the final burn-out
of the char particle and can dominate the composition of the productgas. It will be
shown that, for large particles in a wide range of conditions, these processes cannot
be described by either a homogeneous reaction rate or the shrinking unreacted core
model. Such conditions prevail in moving and fluidised bed gasifiers, as will be
demonstrated for a co-current moving bed biomass gasifier. Therefore a more general
particle model has been used, a local volumetric rate model. It takes into account
that both the chemical reaction rate and the rate of diffusion are functions of the
local char conversion within the particle. The validity of this local volumetric rate
model is demonstrated by experiments determining the local and overall conversion of a
large char particle.

PARTICLE MODELS

The particle model has to describe the heterogeneous reactions of gases and of a
porous reacting solid. The model will be applied to a wide range of gasification con-
ditions and thus has to be flexible enough to take into account.

- complex kinetics such as general order in the gaseous reactant(s), Langmuir
  – Hinselwood kinetics and/or equilibrium reaction systems; and
- reaction rate and diffusivity being a function of the local char conversion (for
  instance due to the changes in the internal pore structure).

Non-catalytic gas-solid reaction models can be divided into structural and volumetric models.

The structural models describe either the internal solid matrix (grainmodels) or the internal pore structure (pore development models) during conversion with a constant surface rate of reaction. Pore development models (e.g. Hashimoto, 1973) take into account that, initially, micropores are created, with subsequent enlargment of existing pores which, later, coalesce. Consequently these models can explain the frequently observed experimental fact that the surface area per unit volume, and thus the volumetric reaction rate, goes through a maximum (Turkdogan, 1970, Beshty, 1978). A problem however, is that too much experimental data are necessary to determine the model parameters indepently and that the surface rate of reaction itself might not be constant. Grain models (e.g. Szekely, 1976) simplify the internal solid matrix to a cluster of regular shaped nonporous grains; the conversion of a grain is described with the shrinking unreacted core model. If diffusion effects can be excluded then, based on an initial grain size, the model predicts a volumetric reaction rate decreasing with increasing char conversion. This predicted decrease is not always equivalent to experimental findings.

As was shown by Chida (1978), the local carbon conversion can be calculated with a grain model based on the local grain size which gives (via the local internal surface area), the local porosity, the reaction rate and diffusivity. Chida ascribes differences between his experimental results and theory to unknown geometrical factors. An analytical volumetric rate model has been presented by Wen (1968). This model predicts the local carbon conversion within the pellet, based on the assumption that the diffusivity and the volumetric reaction rate are independent of the local char conversion. It allows for the shrinking of the pellet. However, their mathematical formulation makes it difficult to allow for other than first order kinetics with respect to the gaseous reactant and zeroth order to the char, but numerical solutions are possible. The advantage of volumetric rate models is that they can use functions relating the reactivity and diffusivity with the conversion, either with or without a structural basis. Thus, as long as the structural models can not predict this functions sufficiently accurate, experimentally found relations should be preferred. It is then practical to relate the reaction rate to the carbon concentration and the diffusivity to the porosity.

THE LOCAL VOLUMETRIC RATE MODEL

For char gasification under our experimental conditions, to be described later, we can make the following assumptions·
1. pseudo-steady state approximation is appropriate for describing the concentration of the gaseous reactants within the pellet
2. external mass transport is excluded here but can be incorporated easily
3. no temperature gradients exists
4. transport of the products out of the pellet has no influence on the diffusion of the reactants and does not influence the process rate.

For the reaction $A + S \rightarrow P$ the rate may be expressed as $-R_A = k\, C_A^n\, C_s^m$ (1) other expressions are possible, however and have been used in the model. The concentration of gas A within the porous pellet is given by

$$D_e(x,t) \frac{d^2 C_A(x,t)}{d x^2} + \frac{a}{x} \frac{d C_A(x,t)}{d x} - R_A = 0 \qquad (2)$$

and the concentration of carbon within the pellet is given by $\dfrac{d C_s(x,t)}{dt} = -R_A$ (3)

with $D_e(x,t) = D * f(\varepsilon)$ (4)
    $\varepsilon = 1 - (1 - \varepsilon_0)\, C_s/C_s(o)$
    a = the geometric factor = o for a slab; 1 for a cylinder, 2 for a sphere.

Boundary conditions.
$x = L$ $C_A = C_{Ao}$, $x = o$ $dC_A/dx = o$, $t = o$ $C_s = C_s(o)$
to allow for shrinking of the particle: $C_s < 0.02\, C_s(o)$ $L = L(t)$.
This set of equations can be solved according to the method of Baker and Oliphant (1960), a three point backwards difference scheme using a linearisation in C_A for the rate equation (1).
To verify this model experiments have been carried out with wood char to find the rate equation (1), the diffusionfunction (4) and the carbon conversion function (3) independently.
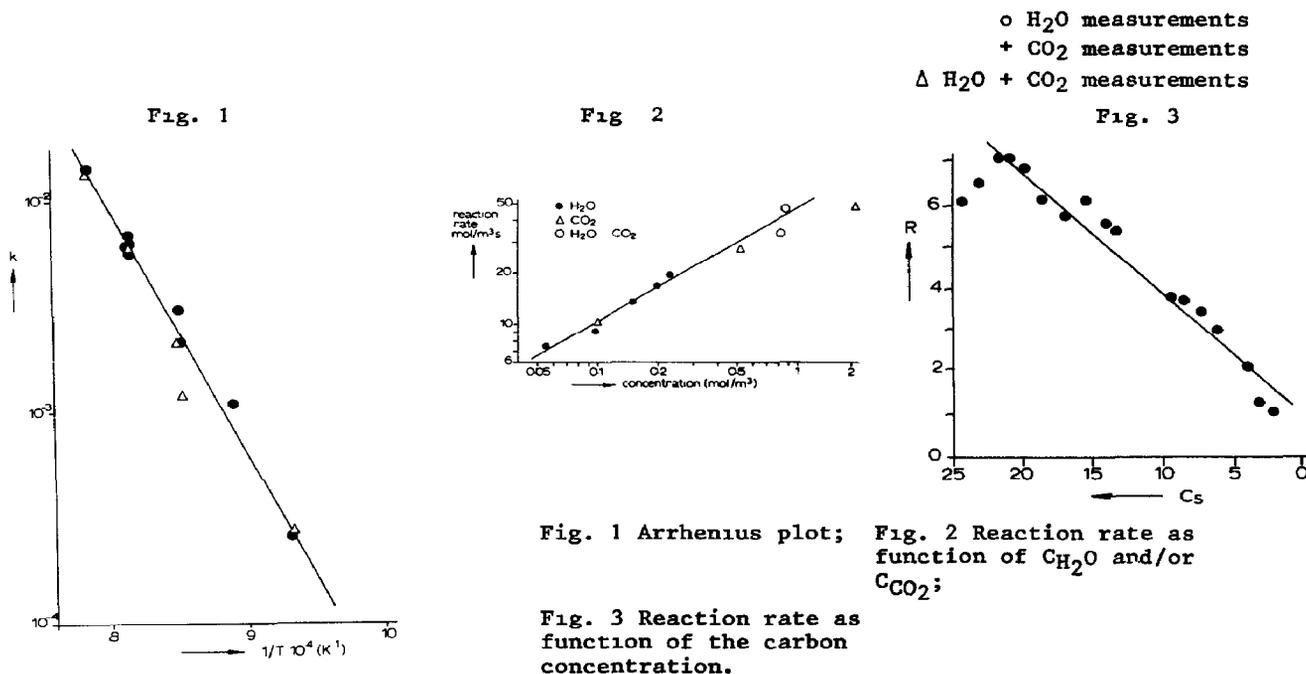
EXPERIMENTAL RESULTS

Reactionrate
Based on thermogravimetric analysis of powdered wood char, the rate expression has
been found for the reaction of carbon with CO_2 and H_2O as a function of the concen-
tration of CO_2 and/or H_2O, the carbonconcentration and temperature, while mass transfer
limitations were excluded (see Fig. 1, 2, 3) (Groeneveld, 1980)
$- R_A = k\ C_s\ (C_{CO_2} + C_{H_2O})^{0.7}$ and $k = A\ exp\ (-\ 217100/RT)$

A may vary from batch to batch from $10^6 - 10^7\ s^{-1}m^{2.1}\ mol^{-0.7}$ allthough the activation
energy and reaction order remain the same.

$o\ <\ C_s\ <\ 25000\ \frac{mol}{m^3}$, $0,05\ <\ C_{H_2O}\ <\ 0.3\ \frac{mol}{m^3}$, $0,10\ <\ C_{CO_2}\ <\ 2.2\ \frac{mol}{m^3}$

$1073\ <\ T\ <\ 1273K$

o H_2O measurements
+ CO_2 measurements
Δ H_2O + CO_2 measurements

Fig. 1   Fig 2   Fig. 3

Fig. 1 Arrhenius plot; Fig. 2 Reaction rate as
                        function of C_{H_2O} and/or
                        C_{CO_2};

Fig. 3 Reaction rate as
function of the carbon
concentration.

Diffusivity
As is pointed out by Turkdogan (1970), wood char has a much larger diffusivity in one
direction than in the other directions. Consequently wood char is described here as a
slab. The diffusivity is measured gravimetically as CO_2 diffuses through the pellet
and absorbs into a concentrated KOH solution (Groeneveld, 1980). It is found that the
diffusivity varies between 0.14 – 0.20 D for an unreacted char particle ($\varepsilon = 0.75$) and
0.70 D for a homogeneous reacted char particle ($\varepsilon = 0.82$).
This rapid increase could be explained by the fast removal of tyloses out of the
macropores, remaining from the capillary wood structure The following relation was
used for 0 75 < ε < 0.84. $D_e = D\ (7.69\ \varepsilon - 5.62)$ and $0.84 \leq \varepsilon < 1$ $D_e = D * \varepsilon$.

Char conversion profiles
With $4 \pm 2 \pm 2\ 10^{-2}$ m wood char particles experiments have been carried out to deter-
mine the carbon concentration as a function of the position within the particle after
exposing it for a certain time to a CO_2/N_2 mixture at temperatures between 973 – 1253 K.
In the experimental set-up, that char particle was cut into slices, piled up again in
a quarts container and the space between the particle and the container filled with
metal slices (see Fig. 4). The container was then put into a quarts tube with a spiral
to preheat the CO_2/N_2 mixture.
This tube was surrounded by an oven. The slices were weighed before and after the
reaction with CO_2 to determine the local carbon concentration. The experimental set-up
was so designed that·
1. external mass transfer of CO_2 had no influence.
   This was tested with water evaporation experiments to determine the Sherwood–

Reynolds relation within this geometry.

2. No temperature gradients existed within or outside the particle. This was tested both from direct measurement of the char temperature and by calculations.

3. Diffusion to the side walls of the particle is neglectable. In one experiment the particle was sliced only after the reaction. Results showed no difference but this technique was more complicated, however.

4. The starting material was homogeneous and weight loss by pyrolyses up to 1250 K was less then 3% in two hours.

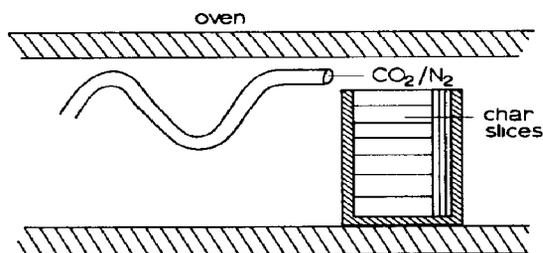In Fig. 5 some experimental results are presented.

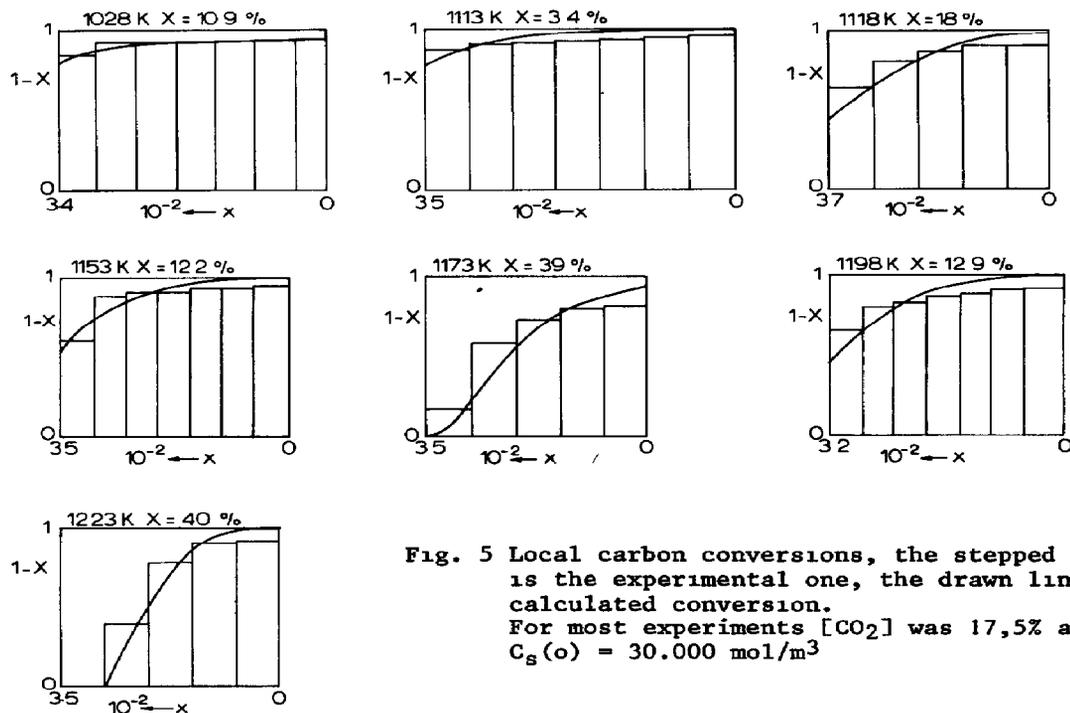Fig. 4 experimental set up to determine local carbon conversions.

Fig. 5 Local carbon conversions, the stepped curve is the experimental one, the drawn line the calculated conversion.
For most experiments $[CO_2]$ was 17,5% and $C_s(o)$ = 30.000 mol/m^3

For the calculations the previously described kinetic and diffusion relations were used. The pre-exponential factor was taken as 0.6 10^6 for all experiments, which was slightly lower than observed in the thermogravimetric analysis

The experimental results on carbon profiles show clearly that the conversion cannot be described accurately with either the shrinking unreacted core or the homogeneous reaction models

The experiments were surprisingly reproducible despite the starting material being made from three different pieces of wood.

TABLE 1   Calculated and experimental residence times belonging to Fig. 5

		overall conversion	t(exp)	t(calculated)
1028	K	10 9 %	21600 s	20170 s
1113		3.4	4500	3690
1118		18.0	20940	19340
1153		12.2	5400	5390
1173		39.0	20460	20620
1198		12.9	2700	2610
1223		40 0	13920	12460

DISCUSSION

The presented results of the model calculations are based on the experimentally found kinetic and diffusivity relations. A single pre-exponetial factor can be used for all experiments Referring to Fig. 5 and Table 1 it can be seen that the model calculations describe accurately both overall and local carbon conversions, it was only at a considerable distance from the particle boundary that experimental conversions were slightly higher than predicted, which, as yet, cannot be explained. It should be noticed that the model presented here can easily be adapted to other kinetic relations and that structural models can be included, in case they predict correctly the volume rate of reaction and the diffusivity as a function of the local carbon conversion.
We used model calculations based on the local volumetric rate model to predict char conversions and char properties in the reduction zone of a co-current moving bed gasifier (Groeneveld, 1979, 1980) (see fig. 6).
In a properly designed gasifier a hot gas containing N_2, CO_2, H_2O and some CH_4 together with char enters the reduction zone. The sensible heat of the inlet flows is used there for the endothermic reactions of CO_2 and H_2O with char
For this application the kinetics in the particle model include the reversible reactions of CO_2 and H_2O with char together with the homogeneous shift equilibrium
$(CO + H_2O = CO_2 + H_2O)$ In the calculations the char particles are assumed to be isotropic spheres.
In practice only at higher conversions the rather anisotropic macro pore structure is more or less broken up, but at present it does not seem justified to take this effect into account.
The particle model is combined with the heat and mass transfer equations describing transfer between the char and the gasphase.
The solids flow is governed by the shrinking of the char particles assuming that char is removed from the outer particle layers when the carbon concentration is less then 2% of $C_s(o)$. The local gas flowrate follows from the mass and heat balance The reduction zone model relates the local values of gas composition, gasflow, temperatures, char properties and the charflow to the inlet conditions.
In table 2 and Fig. 7 experimental results and model calculations are given showing that the model describes the experiments well
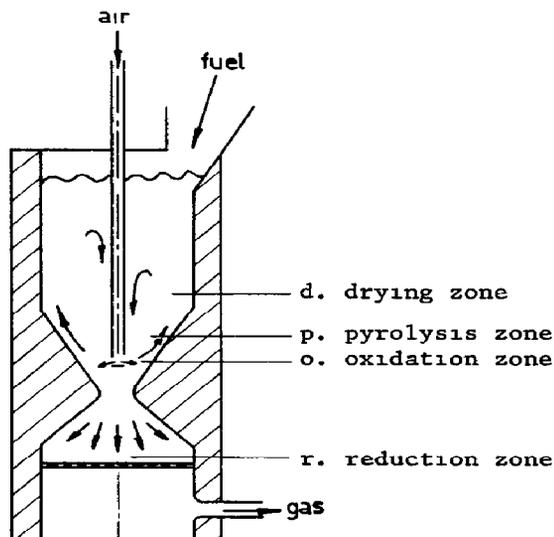

Fig. 6 Co-current Gasifier.

Table 2.

Typical experimental data and results from the reaction
engineering model for the reduction zone

|		exp	calc
In wood	kg/s/m^2	.225	.225
moisture	kg/s/m^2	.036	.036
air	kg/s/m^2	596	596
d_p 10^3	m	24 8	24.8
z	m	0.45	0 53
T air	K	300	300
Out: gas	kg/s/m^2	846	.852
N_2	vol%	49 0	47.5
CO	vol%	15 0	15.3
CO_2	vol%	11.3	12.1
H_2	vol%	13.4	12.4
CH_4	vol%	0.8	0.8
H_2O	vol%	10.5	11.9
ΔH_{in}	kW/m^2	4068	4068
$\Delta H_{chem}/\Delta H_{in}$	%	67	66
$\Delta H_{sens}/\Delta H_{in}$	%		27

Fig. 7. Experimental and calculated conversion, temperature
        and char particle diameter for experiment 1.
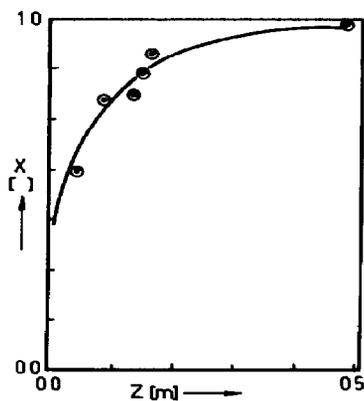
measured and calculated
char conversion in the
reduction zone as a
function of the distance
from the air inlet
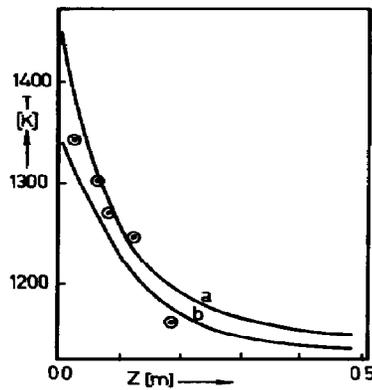
temperature profiles
in the gasifier
⊛ thermocouple measurements
a calculated gas temperature
b calculated char temperature
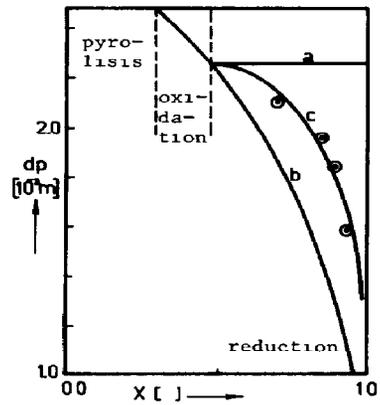
Particle diameter as a function
of the conversion
⊛ measured particle radius
a homogeneous reaction model
b shrinking unreacted core model
c local volumetric rate model

LIST OF SYMBOLS

A	pre exponential factor	$s.m^{3(m+n-1)}.mol^{(1-m-n)}$
a	geometry factor in (2)	—
C	concentration	$mol\ m^{-3}$
D	molecular diffusivity	$m^2\ s^{-1}$
D_e	effective diffusivity	$m^2\ s^{-1}$
k	reaction rate constant	$mol^{(1-n-m)}\ m^{-3(1-n-m)}\ s^{-1}$
L	initial length of particle	m
m	reaction order in S	—
n	reaction order in A	—
P	pressure	kPa
R	gasconstant	$8\ 314\ Jmol^{-1}\ K^{-1}$
R_A	reactionrate of A	$mol\ m^{-3}\ s^{-1}$
T	temperature	K
t	time	s
x	coordinate	m
X	conversion	—
ε	porosity	—

Subscript

A	gaseous reactant A
s	solid reactant (carbon)

REFERECES

- Baker, G.A. and Oliphant, T.A. (1960). An implicit numerical method for solving the two dimensional heat equation. Q. Appl. Math. 17, 4, 361.
- Beshty, B C. (1978). A mathematical model for the combustion of a porous carbon particle. Combust. Flame 32, 295.
- Chida, T. and Tadaki, T. (1978). Modified structural model for solid consuming reaction. J. Chem. Eng. Japan 11, 371.
- Groeneveld, M J. and Van Swaaij, W.P.M. (1979). The design of co-current moving bed gasifiers fueled by biomass. ACS symposium "Thermal conversion of solid wastes, residues and energy crops", September 11-14, Washington D.C..
- Groeneveld, M.J. (1980) PhD. thesis, Twente University of Technology, Enschede, Netherlands.
- Hashimoto, K and Silveston, P.L. (1973). Gasification A.I.Ch.E.J. 19, 159.
- Klass, D.L. (1978) Energy from biomass and wastes, I.G T symposium, August 14-18, Washington D.C .
- Szekely, J., Evans, J W. and Sohn, H.T. (1976) Gas-solid reactions. Academic Press, New York.
- Turkdogan, E.T., Olsson, R.G. and Vinters, J.V.. V (1970) Pore characteristics of carbons, Carbon 8, 545
- Wen, C.Y (1968) Non-catalytic heterogeneous solid fluid reaction models. Ind. Eng. Chem 60, 9, 34