Chemical Engineering Journal 354 (2018) 137–148

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Enhancement of char gasification in CO_2 during chemical looping combustion

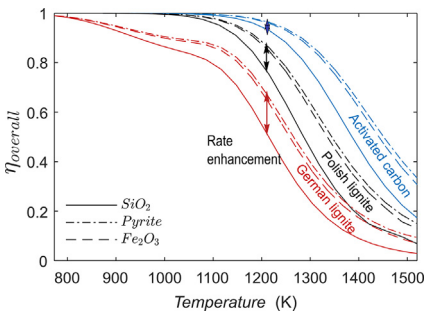
Ewa J. Marek*, Yaoyao Zheng, Stuart A. Scott

Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, United Kingdom

HIGHLIGHTS

- Rate of char gasification increases with temperature and the presence of oxygen carriers.
- Influence from oxygen carriers is significant only if gasification is limited by mass transfer.
- A new expression for the effective rate of char conversion in chemical looping combustion is offered.
- A map of enhancement expected from various oxygen carriers was constructed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Chemical looping combustion
CLC
Gasification
Kinetics
Oxygen carrier

ABSTRACT

Three chars were gasified in CO_2 in a fluidised bed of inert sand or Fe_2O_3 as an oxygen carrier (either derived from an ore or prepared in the laboratory). Rates of gasification were found to increase with temperature and the presence of active oxygen carriers. The observed change varied both with the chars' and carriers' reactivity. A numerical model was developed to simulate char gasification. It accounts for: intrinsic kinetics of gasification, intraparticle mass transfer in the char, external mass transfer in the particulate phase of the fluidised bed and CO combustion in the bed of Fe_2O_3. At 1223 K, CO was removed from the vicinity of the char on being oxidised by an oxygen carrier; this was accompanied by a simultaneous increase in CO_2 concentration, reducing the limitation imposed by mass transfer. It was concluded that the acceleration of gasification by oxygen carriers is significant only if gasification is limited by mass transfer in the first place. In addition, an analytical solution has been proposed, to combine all the processes into one simplified expression for estimating the apparent gasification rate. The influence of the intraparticle resistance was introduced with the effectiveness factor; the gasification rate was linearized with a Taylor series; finally the processes in the particulate phase were described with an enhancement factor, based on the Hatta number. This simple analytical model allows one to predict the influence of an oxygen carrier on the gasification of char during chemical looping combustion. The proposed expression for the effective rate was used to construct a map of the enhancement expected for various kinetic characteristics of an oxygen carrier.

1. Introduction

Direct combustion of a solid fuel by contact with a solid oxygen carrier in chemical looping combustion (CLC) is improbable, at least with typical oxygen carriers, such as Fe_2O_3 [1,2]. In the classical form of chemical looping, conversion of the solid fuel to a gaseous form is

* Corresponding author.
E-mail address: ejm94@cam.ac.uk (E.J. Marek).

https://doi.org/10.1016/j.cej.2018.07.215
Received 23 May 2018; Received in revised form 28 July 2018; Accepted 31 July 2018
Available online 02 August 2018
1385-8947/

Nomenclature

A	Pre-exponential factor in Arrhenius expression for a rate constant (same units as its rate constant)
A_G	Coefficient in the linearized expression for gasification of char (s^{-1})
A_p	Particle surface (m^2)
B_G	Coefficient in the linearized expression for gasification of char (s^{-1})
c_{CO_2}, c_{CO}	Molar concentration of CO_2 and CO ($mol\,m^{-3}$)
C_G	Coefficient in the linearized expression for gasification of char ($mol\,m^{-3}\,s^{-1}$)
d_p	Particle diameter (m)
D_{AB}	Molecular diffusivity ($m^2\,s^{-1}$)
D_e	Effective diffusivity of a gas component ($m^2\,s^{-1}$)
E_a	Activation energy ($kJ\,mol^{-1}$)
F	Enhancement factor (−)
$f(X_{char})$	Function of char conversion, representing relative change in the surface area (–)
$f(X_{OC})$	Function of conversion of oxygen carrier, representing relative change in the surface area (–)
$k_{g,CO}$, k_{g,CO_2}	Mass transfer coefficients ($m\,s^{-1}$)
k_{gm}	Mean mass transfer coefficient ($m\,s^{-1}$)
k_i	Intrinsic rate constant of CO combustion with oxygen carrier (s^{-1})
$k_{Fe_2O_3}$	Apparent rate constant of CO combustion with oxygen carrier (s^{-1})
k_{-1}, k_1	Rate constants per active carbon centre ($mol\,s^{-1}\,bar^{-1)}$
k_2	Rate constants per active carbon centre ($mol\,s^{-1}$)
$K_{p,char}$	Equilibrium constant for char gasification (–)
K_{p,Fe_2O_3}	Equilibrium constant for CO combustion on Fe_2O_3 (–)
M_C	Carbon molar weight ($g\,mol^{-1}$)
N_{CO_2}, N_{CO}	Molar flux of CO_2 and CO ($mol\,m^{-2}\,s^{-1}$)
p_{CO_2}, p_{CO}	Partial pressure of CO_2 and CO (bar)
r_g	Intrinsic rate of gasification ($mol\,g^{-1}\,s^{-1}$)
$r'_{char,max}$	Maximum rate of gasification ($mmol\,s^{-1}\,g^{-1}$)
r_p	Radius of char particle (m)
$r_{p,t}$	Radius of char particle at time t (m)
R	Universal gas constant ($kJ\,mol^{-1}\,K^{-1}$)
R_G	Volumetric rate of gasification ($mol\,s^{-1}\,m^{-3}$)
R_G (X_{char})	Gasification rate at conversion X_{char} ($mol\,s^{-1}\,m^{-3}$)
$R_{G,eff}$	Effective rates of gasification ($mol\,s^{-1}\,m^{-3}$)
R_p	Particle radius of oxygen carrier (m)
R_{OC}	Rate of CO combustion with oxygen carrier ($mol\,s^{-1}\,m^{-3}$)
Sh	Sherwood number (–)
Sh_0	Constant in Eq. (19)
U_{mf}	Minimum superficial fluidising velocity ($m\,s^{-1}$)
Greek letters	
δ	Thickness of the mass transfer boundary layer (m)
γ	Hatta number (–)
ε_{char}	Char porosity
ε_{mf}	Voidage in the particulate phase (–)
ρ_{char}	Char molar density ($mol\,m^{-3}$)
η	Radial position after coordinate transformation (–)
η_{char}	Effectiveness factor for gasification of char (–)
$\eta_{Fe_2O_3}$	Effectiveness factor for Fe_2O_3 reduction (–)
$\eta_{overall}$	Overall effectiveness of char gasification
ν	Kinematic viscosity ($m^2\,s^{-1}$)
τ	Tortuosity (–)
Φ	Thiele modulus (–)
Subscripts	
bulk	In the bulk
char	In regards to the gasification of char
Fe_2O_3	In regards to CO combustion with oxygen carrier
s	Particle surface

required, and the gaseous product combusts in a reaction with an oxygen carrier. Alternatively, carriers, which release oxygen into the gas phase can be used, as in the CLOU process, allowing for a direct combustion of the solid fuel [3].

Conversion from a solid to a gaseous fuel can involve gasification by CO_2 or H_2O prior to combustion with an oxygen carrier or gasification carried out *in-situ* in the fuel reactor [4,5]. In both cases, if gasification takes place at moderate temperatures and low pressures, it is relatively slow, which will most likely limit the overall rate of CLC [2,6,7]. Besides the slow conversion of fuel, finding suitable oxygen carriers could also be problematic. Lyngfeld [8] suggested that the implementation of CLC with solid fuels at industrial scale will require inexpensive, naturally occurring minerals to be used as oxygen carriers. This is mostly due to the quick deactivation of the oxygen carrier in the presence of impurities carried by the solid fuel. A large makeup of material is needed, which is uneconomic unless cheap oxygen carriers can be found [9].

Finally, the effective performance of solid fuel gasification during CLC may not be easy to predict. The result depends not only on the fuel's properties and process parameters, as in the conventional combustion but also on the properties of the oxygen carrier. These, however, are rarely reported together, as a complementary set of attributes describing a CLC setup. Gasification, in the presence of an oxygen carrier, can be influenced by the combustion of a gaseous product, which makes the overall process challenging to assess. Previous studies report that an increase in the rate of char conversion was observed during the in-situ gasification in CLC [10]. Saucedo *et al.* [6] suggested that the acceleration of the observed rate is connected only to mass transfer, which often controls gasification. If a very reactive fuel is gasified in the diffusion-controlled-regime, the consumption of the gasification products by the oxygen carrier may reduce the mass transfer restriction. This was supported by the fact that the gasification rate was not increased if the process was carried out at low temperatures, where it was instead limited by slow reaction kinetics.

So far, the main conclusion is that the enhancement depends on a set of conditions, at which gasification takes place. Process parameters, oxygen carrier's reactivity and kinetics of char gasification – all must be considered. This study analysed the problem comprehensively. First, the kinetics of char gasification in CO_2 and the kinetics of CO combustion with oxygen carrier were evaluated separately. Then, the gasification of char in CO_2 was carried out in the presence of oxygen carrier, as in chemical looping. Finally, for the combined situation: *in-situ* gasification of char and combustion of the gasification product using an oxygen carrier, we proposed a simplified model to quickly evaluate the effective rate of gasification.

2. Experimental

2.1. Fuels and bed materials

Three fuels were used in the gasification experiments: activated carbon, and two lignite chars: Polish char and a German char. The first one, a relatively unreactive activated carbon (Sigma-Aldrich C2889, peat bog char), was only crushed and sieved to 650–800 μm prior to the experiments. The last two fuels were prepared from Polish lignite coal (Belchatow area) and German Hambach lignite coal. Coals were pyrolysed in a fluidised bed (i.d. 78 mm) in a continuous flow of hot nitrogen at 1173 K for 2 h. Then the bed was cooled to room temperature, also in N_2. Resulting chars were sieved to 650–800 μm. The German char was prepared and described by Saucedo [11]. The proximate