Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 2219–2233

www.elsevier.com/locate/jeurceramsoc

Corrosion of ceramics for vinasse gasification in supercritical water

Thierry Richard [a,*], Jacques Poirier [a], Cedric Reverte [b], Cyril Aymonier [b], Anne Loppinet-Serani [b], Gökalp Iskender [c], Escot-Bocanegra Pablo [c], Frederic Marias [d]

[a] CEMHTI - Conditions Extrêmes et Matériaux: Haute Température et Irradiations, CNRS, Université d'Orléans, 1b avenue de la recherche scientifique, 45071 Orléans, cedex, Orléans, France

[b] ICMCB, Institut de Chimie et de la Matière Condensée de Bordeaux, Université de Bordeaux, CNRS, 87 avenue du Dr. A. Schweitzer, Pessac F-33608, France

[c] ICARE, Institut de Combustion, Aérothermique, Réactivité et Environnement, CNRS, 1c avenue de la recherche scientifique, 45071 Orléans, France

[d] LATEP, Laboratoire de Thermique, Energétique et Procédés, Rue Jules Ferry, 64000 Pau, France

Received 14 September 2011; received in revised form 17 February 2012; accepted 2 March 2012
Available online 5 April 2012

Abstract

Supercritical water gasification (SCWG) is a very efficient process to convert wet biomass into energetic gases. Unfortunately, SCWG reactor may strongly corrode due to the addition of temperature, pressure and the presence of corrosive species. In the present paper, the corrosion of various ceramic materials in subcritical and supercritical water (SCW) gasification process was studied in a batch reactor. We compare the corrosion in distillated water and the corrosion in sugar beet slurry that will be gasified under supercritical conditions. The experimental temperatures were 350 °C and 550 °C and the pressure was 25 MPa. Technical ceramics (SiC, alumina, Y stabilized zirconia, Si_3N_4, BN, aluminosilicate, cordierite-mullite) show poor capability to sustain corrosion whereas graphite and glassy carbon are the highest performance materials in our working conditions.

Keywords: Corrosion; Supercritical water gasification; Ceramics; Wastewater

1. Introduction

Supercritical water (critical point: $T_c = 374\,°C$ and $P_c = 22.1$ MPa) is a favourable medium for chemistry applications. It has current applications in the field of bioenergy, organics destruction or material synthesis.[1–3] Supercritical water biomass gasification (SCBG) is an innovative and efficient way to convert humid biomass into a gas with a great heating value ($CO + H_2$ and/or methane).[1] Contrary to supercritical water oxidation process (SCWO), supercritical water gasification process (SCWG) operates in a very poor oxygen environment. In these conditions, organic matter decomposes mainly into H_2, CH_4, CO, and CO_2 under the effects of both pyrolysis and hydrolysis reactions.[4,5] Regarding the temperature these reactions can also lead to numerous organic molecules recovered at the end of the process in the liquid phase.[6] The reactions involved are quite complex even in the case of simple and well-known organic molecules like glycerol, glucose or formic acid.[5,7,8]

This SCWG process has many economic and environmental advantages:

(1) biomass can be converted without drying, which would be prohibitive for the overall energy balance;
(2) in supercritical water, most of the organic compounds become soluble;
(3) the overall reaction kinetics are very efficient due to the high diffusivity in supercritical mixtures and generally homogeneous reaction medium;
(4) compared to "classical gasification", SCWG is a low temperature process so no polycyclic aromatic hydrocarbons, no NOx and no SOx are produced;
(5) the produced gas is hydrogen rich.

The SCBG process can combine the action of pressure and temperature in complex fluids containing corrosive species (for instance chlorides and alkali) in different concentrations. Material corrosion is a challenge in SCWG due to the feedstock

* Corresponding author. Tel.: +33 238 256 688; fax: +33 238 638 103.
E-mail address: thierry.richard@cnrs-orleans.fr (T. Richard).

0955-2219/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2012.03.007

variability. The use of metal and alloys to build gasification reactors is limited for three main reasons:

(1) The creep at quite elevated pressure (30 MPa) limits the working temperature around 600 °C. Over this limit the mechanical strength decreases and materials do not sustain pressure anymore. Actually, the creep resistance depends on the alloys mechanical properties and on 3 external parameters: temperature, pressure and time. For creep resistance, there is an equivalency between the time and the temperature. At a given pressure, if the temperature increases then the rupture life decreases. At the opposite if we want to increase the rupture lifetime we have to reduce the temperature conditions. Commercial reactors must be designed for a long time of utilization (100,000 h) it defines the temperature and pressure limit.
(2) Material grade must also be chosen with care because some type of alloy cannot sustain every corrosive condition.[9]
(3) As outlined by Kruse,[10] hydrogen is known to be able to change the mechanical stability of metals. Direct interaction between H_2 and materials cannot be excluded and the action of a highly concentrated H_2 atmosphere may be destructive for metals.

Corrosion is known to be more severe in near-critical water than in supercritical water. In this near-critical region water density, ionic product and temperature are high enough to influence chemical reactions.[9] However, significant corrosion may occur in supercritical conditions even if ionic reactions are not supported. Solid salt deposits can create a local corrosive environment where water or brine can be trapped between the solid layer and the wall. At higher temperature, molten salt can also be corrosive. Material corrosion is a serious issue in supercritical water processes because strongly oxidizing (SCWO) or more reducing (SCWG) conditions can be created.[11]

Many studies are devoted to metallic or alloys corrosion in SCW. Most of them are parametric studies of corrosion in SCWO conditions, in the presence of oxygen, acids and salts.[12–16] Nickel-based alloys are preferred for such applications because of their chemical and mechanical stress resistance at both elevated temperature (from ambient up to 600 °C) and pressure (30 MPa). Hwang et al.[17] outlined the highest performance of Ni alloys compared to Ferritic/Martensitic steel in deionized supercritical water. Anyway, corrosion is dependent upon environmental factors (density, temperature, pH, electrochemical potential, presence of anions and heat treatments) and on material characteristics (alloy composition, purity, surface properties).[9] The corrosion resistance of metals and alloys can be explained by passive oxide film formation on their surfaces. In supercritical water gasification condition, oxide film stability may be limited by the formation of reductive gas (H_2, CH_4). In low electrochemical potentials, active dissolution of many metals (Fe, Ni, Cr, etc.) may occur.[11] D'Jesus et al.[18] observed the reduction of a NiO passivating film formed on the surface of 625 nickel alloy at only a few bars of hydrogen partial pressure although thermodynamical calculation shows that it should happen at higher partial pressure (10 MPa). The specificity of SCWG and the different types of corrosion encountered are outlined by Marrone and Hong.[11] Kruse[10] reports that nickel-based alloy 625 was used for more than 1000 h in SCWG experiments with methanol and that hydrogen formation does not seem to be problematic for gasification reactor under these experimental conditions. Sometimes corrosion was found due to the presence of sulfur or K_2CO_3 in the reacting media.[10] On the other hand, a significant corrosion of nickel-based alloys (including Inconel® 625 and Hastelloy C276) had been reported by Calzavara et al.[19] Obviously, there is no universal material that could withstand all types of biomass in every set of operating conditions.

Ceramics are very resistant under extreme conditions and may be considered as material to build an anticorrosive wall for biomass gasification reactors. Few papers are devoted to ceramic behavior in hydrothermal environments. As hydrothermal oxidation is very efficient to treat hazardous compounds, dioxins, and to destroy halogenated species,[20] ceramic corrosion has been studied for the supercritical water oxidation process in the presence of acidic or chlorinated species. Boukis et al.[21] show a screening test of high performance ceramics in supercritical water containing oxygen and hydrochloric acid. In this paper 33 ceramics have been studied. Other papers devoted to the corrosion of technical ceramics like SiC,[22,23] Si_3N_4,[21] alumina,[24] zirconium oxides[25] can be found in the literature. All of them deal with specific conditions related to SCWO. Unfortunately, all results obtained in an oxidative environment may be of poor interest in the case of reductive conditions.[11] To our knowledge, there are only a few papers dealing with material corrosion in SCWG and none that discusses the specific use of ceramics.[11]

The aim of this paper is to study the corrosion behavior of various ceramic materials and carbon (graphite and glassy carbon) materials in subcritical and supercritical water biomass gasification in a batch reactor. The real biomass used in this study is sugar beet slurry also called "vinasse".

2. Experimental

2.1. Materials

The fluid used is either distilled water or sugar beet slurry called "vinasse". The high water content and the high organic concentration make this resource reliable for the supercritical water biomass gasification (SCBG) treatment. The global composition of this slurry is given in Table 1. A quantitative analysis of atomic species has been performed by ICP-OES (720ES – Varian Company). Anions have been characterized by liquid chromatography using the Dionex DX-120 chromatograph with ion pac AS14A and AG14A column. The eluent was a mix of $NaHCO_3$ and Na_2CO_3. The results are presented in Table 2.

During the supercritical water treatment, organic materials from biomass are converted into gas, liquid and solid phase whose balance depends especially on temperature. The composition of the liquid phase (water soluble and insoluble species) in such converted biomass with SCBG is generally complex as reported elsewhere by Carrier et al.[6] The gas contains reductive species (like H_2 or CH_4) and forms a reactive atmosphere that may lead to materials corrosion. In gasification the