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Design and operation of pilot plant for CO_2 capture from IGCC flue gases by combined cryogenic and hydrate method

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ABSTRACT

This project is a trial conducted under contract with CO_2CRC, Australia of a new CO_2 capture technology that can be applied to integrated gasification combined cycle power plants and other industrial gasification facilities. The technology is based on combination of two low temperature processes, namely cryogenic condensation and the formation of hydrates, to remove CO_2 from the gas stream. The first stage of this technology is condensation at −55 °C where CO_2 concentration is expected to be reduced by up to 75 mol%. Remaining CO_2 is captured in the form of solid hydrate at about 1 °C reducing CO_2 concentration down to 7 mol% using hydrate promoters. This integrated cryogenic condensation and CO_2 hydrate capture technology hold promise for greater reduction of CO_2 emissions at lower cost and energy demand. Overall, the process produced gas with a hydrogen content better than 90 mol%. The concentrated CO_2 stream was produced with 95–97 mol% purity in liquid form at high pressure and is available for re-use or sequestration. The enhancement of carbon dioxide hydrate formation and separation in the presence of new hydrate promoter is also discussed. A laboratory scale flow system for the continuous production of condensed CO_2 and carbon dioxide hydrates is also described and operational details are identified.

Keywords: CO_2 abatement; Carbon capture; IGCC; Cryogenic condensation; CO_2 hydrate; Hydrate promoter

1. Introduction

Environmental concerns make development of an economically viable technology for CO_2 capture essential to continuation of the utilisation of fossil fuels for power generation. The integrated gasification combined cycle (IGCC) utilises low value fuel ranging from coal to municipal waste for high quality power generation. The major benefit of this cycle is the potential for zero greenhouse gas emissions. There are basically two well established variations for IGCC plant arrangement, using correspondingly Shell and GE (Texaco) gasification processes. In the first arrangement, dry ground coal is gasified under a pressure of about 3 MPa, and high heat recovery is achieved due to generation of high pressure steam in a heat recovery boiler used for cooling of the raw gas stream. The GE IGCC plant features a slurry feed gasifier, operating at a pressure between 5 and 6 MPa combined with subsequent water quench. Although additional energy is required for water evaporation in the latter case, the total energy penalty for CO_2 capture is lower due to generation of sufficient steam for shift-conversion (Zheng and Furinsky, 2005; Klara and Wimer, 2007).

Capture of CO_2 by hydrate from a shifted syngas stream project based on the low temperature SIMTECHE/Nexant process was launched by the US Department of Energy (DOE) in 1999, and experimental testing in a continuous flow hydrate reactor commenced in 2001 (Project Fact Sheet US DOE, 2002). Utilisation of multi-step CO_2 hydrate formation was shown to be capable of capturing 68% CO_2 from syngas at a single pass in the presence of hydrogen sulphide and pure water. A continuous flow reactor was designed and constructed, and the feasibility of hydrate formation in a flow-through system was confirmed. The reactor was operated at near water freezing temperatures and pressures between 750 and 2200 psi at

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which hydrate slurry was formed. It was claimed that overall capture rate can be increased up to 90% using ammonium salts additives as promoters (Figueroa et al., 2004; Plasynski et al., 2008). Unfortunately, there are no data available on the application of promoters other than H_2S within this project.

A similar method for CO_2 separation from IGCC flue stream by means of catalytic hydrate formation has been studied at the Chinese Academy of Science (Li et al., 2010). Tetra-butylammonium bromide (TBAB) was used to shift hydrate equilibrium conditions towards lower pressure at the same temperature and increase the efficiency of capture. The best result shows 54% capture of CO_2 from the feed gas mixture consisting of 60.8 mol% hydrogen and 39.2 mol% carbon dioxide by a single stage. In the second stage hydrate is formed from 18 mol% CO_2–H_2 gas mixture, and the pressure–temperature conditions can be brought up to 284 K at 5 MPa by means of using 1 mol% TBAB solution. No data are reported regarding the final possible CO_2 separation.

Hydrate based gas separation (HBGS) in the presence of tetrahydrofuran, according to the authors, offers the capability of capturing 99 mol% CO_2 from the flue stream (Kang and Lee, 2000).

Cryogenic condensation of CO_2 from a mixture of gases, e.g. Ryan–Holmes process (Holmes and Ryan, 1982a,b), is a well established technique for purification of natural gas from carbon dioxide. The CryoCell technology (Amin et al., 2005), the latest improvement made to the natural gas sweetening process, is implemented at the Cool Energy demonstration site in Dongara, Australia launched in 2006. Extensive studies have been conducted on separation of hydrocarbon mixtures containing 5–95 mol% CO_2, and numerous improvements have been made since this technology was first introduced. Plenty of experimental data are tabulated and plotted on graphs showing phase envelopes of CO_2–hydrocarbons mixtures, however only limited information is available on application of cryogenic condensation for large-scale separation of CO_2–hydrogen mixtures.

Cryogenic condensation has been proposed at Brigham Young University by Dr. Larry Baxter for post-combustion CO_2 capture from power plants (Baxter, 2009). Relatively low-CO_2 content in the feed, less than 15 mol%, and pressure slightly above atmospheric dictates the use of temperatures in the order of −120 to −135 °C. At these temperatures, CO_2 forms a solid and, therefore, does not contain any substantial amount of impurities. Capture rates as high as 90–99 mol% CO_2 are claimed to be achievable using this technology.

Table 1 – Coal composition used in the IGCC.

Component	Composition (wt%)
Inherent moisture	9.5
Ash	12.2
Carbon	64.5
Hydrogen	4.38
Nitrogen	1.41
Oxygen	7.04
Sulphur	0.86
Chlorine	0.02
LHV (MJ/kg)	25.87

In this work we are presenting the results of a combination of experimental and simulation studies on the integration of the cryogenic process with the synthetic hydrate process for the separation of CO_2 from syngas. The work includes details of the pilot plant design and operation.

2. Background

The composition of the process gas depends on the type of coal used by the process and the operating conditions. Based on Australian bituminous coal the process gas has been identified with respect to its composition for both the GE and Shell processes. The Australian coal has the following composition (Table 1).

Chilled flue gas after the gasifier is purified from COS by hydrolysis and from H_2S by chemical absorption. Raw gas containing mainly CO, hydrogen and steam with small inclusions of CO_2 and inerts is passed through the shift-converter. Process gas compositions and process conditions after shift-conversion based upon the IGCC GE and Shell processes selected for this study are shown in Table 2. The values were calculated for 500 MW power generating plant utilising IGCC combustion technique with 38% overall efficiency. Figures presented here agree well with other combustion flue gas data available in the literature. Existing technologies for CO_2 capture such as physical and chemical absorption, adsorption and membranes perform satisfactorily for up to 90 mol% capture of CO_2, however the associated costs need to be reduced. For example, separation of nearly all hydrogen from the shifted gas stream by membrane with further CO_2 condensation is patented (Reddy et al., 2004). Abatement rates are improved to 90 mol% CO_2 (Forsyth et al., 2009) capture. In this patent, a hydrogen-rich stream containing 10 mol% CO_2 is obtained, however the separated liquefied CO_2 is of only 63–70 mol%

Table 2 – IGCC GE and Shell compositions and conditions (dry basis).

Component	Process stream composition (mol%)			
	IGCC GE		IGCC Shell	
	Initial	Corrected without H_2S and CH_4	Initial	Corrected without H_2S and CH_4
H_2	55.145	58.131	56.686	59.312
CO[a]	2.845		2.52	
CO_2	40.3	40.397	37.025	37.092
N_2	0.681	0.682	3.11	3.115
CH_4	0.02		0	
H_2S[a]	0.22		0.181	
Ar	0.7915	0.792	0.481	0.481
Inlet pressure	57.2 bar		53 bar (supplied at 28.3 bar in process)	

[a] CO and H_2S have been eliminated for this experimentation due to safety reasons.