Fuel Processing Technology 174 (2018) 78–87

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Absorption kinetics of mercury (II) chloride into water and aqueous sodium chloride solution

Fenny Kho, Gia Hung Pham*

Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth 6845, Australia

ARTICLE INFO

Keywords:
Mercury (II) chloride absorption
Kinetics
Two-film theory
Mercury analysis
Mass transfer

ABSTRACT

Mercury has been reported to be naturally occurring trace contaminant in the oil and gas reservoirs. In this study, the absorption characteristic of mercury (II) chloride ($HgCl_2$) in water and aqueous sodium chloride (NaCl) solution was investigated. The kinetic parameters of the reaction between $HgCl_2$ and NaCl is reported for the first time. A semi-batch reactor is used in this work to investigate the absorption process. The solid vaporization method is applied to generate $HgCl_2$ gas at different concentrations for this study. At the same hydrodynamic condition, the absorption flux of $HgCl_2$ into water increases from 6.02×10^{-6} to 10.26×10^{-6} mol/m^2.h when absorption temperature is increased from 298 to 333 K. Applying the two-film theory, the absorption of $HgCl_2$ into water is controlled by the gas phase resistance. The mass transfer coefficient k_G does not change with the $HgCl_2$ concentration in the gas phase significantly, but is affected by the absorption temperature. For the case of absorption of $HgCl_2$ into aqueous NaCl solution, the absorption flux increases with increasing NaCl concentration and absorption temperature. The mechanism of reaction between $HgCl_2$ and NaCl is proposed and the reaction rate law follows second order; first order with respect to $HgCl_2$ and Cl^- with the reaction rate constant $k_2 = 1.09 \times 10^9 \exp\left(\frac{-123.32\ \text{kJ / mol}}{RT}\right)$ m^3/mol·s.

1. Introduction

Mercury has been reported to be naturally occurring trace contaminant in the oil and gas reservoirs [1], with varying mercury species and concentration levels depending on the geological location [2]. Mercury species exist in natural gas and crude oil in three main groups, namely elemental mercury (Hg°), organic mercury such as dimethyl mercury (DMM) and inorganic mercury such as mercury (II) chloride ($HgCl_2$) and mercury (II) sulphide (HgS) [2,3]. The physical and chemical properties of mercury species are different, therefore they behave differently in oil and gas processes. In addition, mercury pollutants in the environment come from incineration of municipal solid waste and coal; at high temperatures ($>$ 1073 K), mercury exists in the flue gas as Hg^0 as this mercury species is reactive and reacts with available Cl_2 in the flue gas to yield inorganic mercury $HgCl_2$. The flue gas escapes the incineration process at about 573 K with the typical mercury concentration ranges between 200 and 2000 μg/Nm^3 [4,5].

In the liquefied natural gas (LNG) processing, after the natural gas primary separation in a slug catcher, mercury species were detected in all three phases (gas, condensate and water phase). The total mercury in the gas, condensate and water phase have been reported to vary widely from $<$ 0.01–5000 μg/Nm^3, $<$ 0.001–6 mg/l and $<$ 0.001–0.3 mg/l respectively in several well-known gas fields [6–10]. The mercury species detected in the gas phase are namely, Hg°, DMM, dibutyl mercury, diphenyl mercury and $HgCl_2$; Hg° being the dominant species [3,11,12]. The main mercury species detected in the condensate phase are Hg°, DMM, $HgCl_2$, suspended HgS and CH_3HgCl; $HgCl_2$ has been found to be the dominant species [2,3,13,14]. In the water phase, $HgCl_2$ exists as the main mercury species [15]. Usually, untreated water phase is released from natural gas process and this becomes one of the major ways mercury enters the environment [15]. Although the concentration is quite low, mercury species have the tendency to accumulate in the process by adsorption, chemical reaction, dissolution in sludge and condensation [1], causing several detrimental effects such as damaging liquefaction heat exchanger, corrosion, catalyst poisoning, and technical plant maintenance. Therefore, it is important to conduct complete mercury mapping and perform mercury balance for oil and gas processes to determine the mercury pathway in the process and their impact on the different products (gas and condensate) and waste streams. Understanding how each of the mercury species behave at different stages is also critical to make sure the safeguards are put in place to perform operations and maintenance in the field as well as environmental protection strategies if required.

With the current energy demand, an increasing number of LNG

---

* Corresponding author.
E-mail address: g.pham@curtin.edu.au (G.H. Pham).

https://doi.org/10.1016/j.fuproc.2018.02.017
Received 15 December 2017; Received in revised form 14 February 2018; Accepted 14 February 2018

Nomenclature

J	Absorption flux, mol/m^2·s
K_L	Overall liquid mass transfer coefficient, m/s
k_L	Liquid side mass transfer coefficient, m/s
k_G	Gas side mass transfer coefficient, mol/Pa.m^2·s
He	Henry coefficient, Pa.m^3/mol
He_T	Henry coefficient at temperature T, Pa.m^3/mol
He_{298K}	Henry coefficient at 298 K, Pa.m^3/mol
T	Temperature, K
C_L	Concentration in the bulk liquid side, mol/m^3
C_L^*	Equilibrium concentration at liquid side interface, mol/m^3
$-r_{HgCl_2}'''$	Rate of absorption of $HgCl_2$ into the liquid, mol/m^3·s
a	Ratio between gas/liquid interface area and volume of reactor, m^2/m^3
C_{Cl^-}	Concentration of Cl^- ions in the liquid, mol/m^3
f_l	Ratio between volume of liquid and reactor, dimensionless
P_{HgCl_2}, g	Partial pressure of $HgCl_2$ in the gas phase, Pa
k_2	Second order rate constant, m^3/mol·s
E_a	Activation energy, kJ/mol
R	Gas Constant, 8.314 J/mol·K

plants are in operation around the world. The increasing volume of natural gas being extracted will contribute to the increasing mercury levels in the environment [16,17]. An additional source of mercury accumulation in the environment includes $HgCl_2$ released in exhaust gas from burning coal and heavy oil. Absorption into water by means of gas-liquid contactor has been developed and can be an effective way to remove $HgCl_2$ from flue gas [18].

Mercury species can be transferred between gas and water phase in the LNG process at different stages, such as gas separation in slug catcher, monoethylene glycol (MEG) regeneration and acid gas removal using amine solution. Being the major species found in the fossil fuels and environment, Hg° is very well studied [19,20], however there is a lack of information about organic and inorganic mercury available. With the current mercury problems and knowledge standpoint, the information with regards to the kinetics of absorption of each mercury species, especially $HgCl_2$ is needed urgently to enable the prediction of the dynamics of mercury accumulation in oil and gas processing equipment and mercury behaviours in flue gas treatment process using absorption technique at any given time.

Several work has been done to close the knowledge gap with regards to $HgCl_2$ behaviour such as the saturated solubility in different solvents [21], distribution between gas and liquid system and Henry coefficient [22,23]. To the best of our knowledge, the solubility information on $HgCl_2$ is currently limited to either saturated or equilibrium condition, and no information available for its absorption kinetics.

This work focuses on the absorption kinetics of $HgCl_2$ gas into water and aqueous NaCl solutions at different temperatures (298–333 K) and NaCl concentrations (0.5–3.5 wt%) using a bench scale semi-batch reactor system. A suitable quantitative analysis of $HgCl_2$ in gas and water phase for absorption kinetics study is also discussed. Furthermore, the reaction mechanism for the reaction between $HgCl_2$ (g) and NaCl (aq) is proposed. Finally, the Two-Film theory will be used to model the reaction and calculate the reaction kinetics constant.

2. Methodology

2.1. Generation of mercury (II) chloride feed gas

There is no certified commercial $HgCl_2$ test gas cylinder available in the market, therefore the test gas needs to be freshly generated for all test in this study on the solubility kinetics of $HgCl_2$ gas in water.

Generation of constant source of $HgCl_2$ gas using the principle of temperature-controlled dynamic generation from pure solid in a tube or container has been successfully utilised to produce constant $HgCl_2$ gas concentration for different research objectives with error reported ranging from 1 to 23% [24–28]. In this work, the same principle is used to produce desired $HgCl_2$ gas concentrations. In short, a required dry $HgCl_2$ solid amount (≥99.5%, Sigma Aldrich) was placed inside a 125 ml cylindrical glass vessel (ID: 40 mm, Height: 155 mm) MF 29/3/125 Quickfit Drechsel bottle; distributed in the middle of a quartz wool as a fixed bed to keep $HgCl_2$ solid surface area for vaporization constant. Prior to the test, the vaporization vessel was placed in a temperature controlled water bath at least 2 days to ensure no temperature gradient exists in the vaporizer. This is done in which the carrier gas (UHP N_2, 99.999% purchased from BOC) is sent to the bottom of the vaporizer and distributed by a fritted quartz disk. The flow rate of the carrier gas was set at 500 ml/min for all the test in this work and controlled by a mass flow controller (MFC) to ensure constant supply of $HgCl_2$ gas concentration throughout the test. The $HgCl_2$ contaminated gas left the vaporizer at the top of the bottle (please see Fig. 1). The

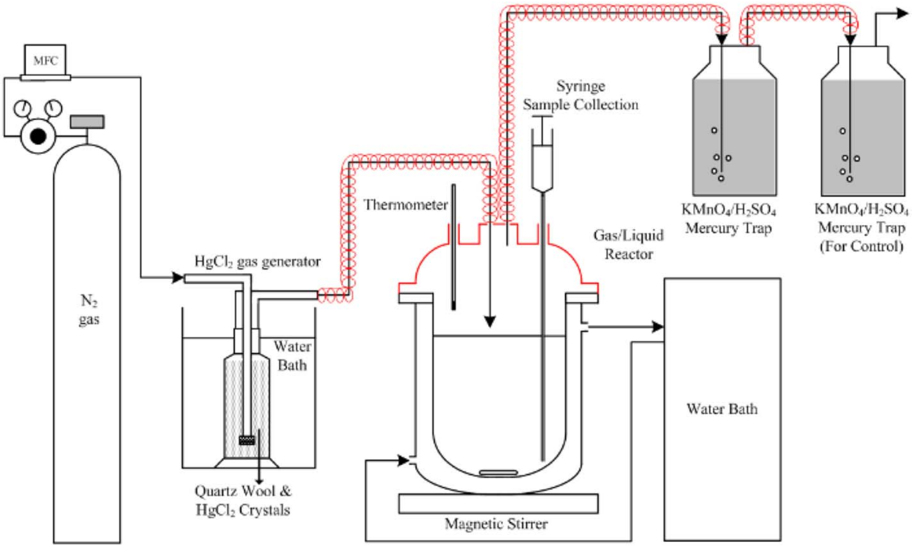

Fig. 1. Experimental set-up for $HgCl_2$ absorption kinetics study.