

PROPOSED CO₂ HYDRATE TECHNOLOGY APPLICATION FOR CARBON CAPTURE AND STORAGE IMPLEMENTATION IN INDONESIA

USULAN PENERAPAN TEKNOLOGI HIDRAT CO₂ UNTUK IMPLEMENTASI PENYERAPAN DAN PENYIMPANAN KARBON DI INDONESIA

Yusep Kartiwa Caryana

"LEMIGAS" R&D Center for Oil and Gas Technology
Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, P.O. Box 1089/JKT, Jakarta Selatan 12230 INDONESIA
Tromol Pos: 6022/KBYB-Jakarta 12120, Telephone: 62-21-7394422, Faxsimile: 62-21-7246150
E-mail: yusepkc@lemigas.esdm.go.id, E-mail: cepyusepkc@gmail.com

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ABSTRAK

Penyerapan dan penyimpanan karbon atau Carbon Capture and Storage (CCS) perlu dilaksanakan pada berbagai bidang pembangunan termasuk industri hilir minyak dan gas bumi karena pemerintah Indonesia telah mengadopsi Perjanjian Paris tentang Penurunan Emisi Gas Rumah Kaca (the Paris Agreement on Greenhouse Gas Emissions Reduction). Berbagai teknik penyerapan emisi CO₂ hasil pembakaran telah dikembangkan. Salah satu pendekatan baru untuk menyerap CO₂ guna mengurangi emisi ke atmosfer adalah teknologi (kristalisasi) hidrat gas CO₂. Dasar dari teknologi hidrat CO₂ adalah seleksi parsial terhadap komponen-komponen target fasa hidrat dan fasa gas. Dengan teknik ini, ditargetkan CO₂ dapat lebih mudah dijebak dan ditangkap ke dalam fasa kristal, dibanding komponen lain. Studi terdahulu menemukan bahwa kesetimbangan gas/hidrat masing-masing pada tekanan 7,6 MPa dan 11,0 MPa serta temperatur 274 K dan 277 K, tidak tepat diterapkan pada industri hilir minyak dan gas bumi karena akan diperlukan biaya yang sangat tinggi untuk mengompresi gas sampai dengan tekanan pembentukan hidrat. Promotor hidrat yang tepat termasuk tetrahydrofuran (THF) dan sodium dodecyl sulfate (SDS) dapat digunakan supaya tekanan pembentukan hidrat dan konsumsi energi yang optimal dapat dicapai sesuai realitas industri. Dengan menambahkan THF dan SDS sekitar 62,3 Nm³/m³ hidrat CO₂ dapat terbentuk pada tekanan 30 bar dan temperatur antara 274 – 277 K dalam waktu reaksi sekitar 15 menit. Hasil berbagai eksperimen menunjukkan bahwa dengan jaminan kontak cairan dan gas serta promotor hidrat yang optimal, teknologi pembentukan hidrat CO₂ secara berkelanjutan akan layak diterapkan pada skala industri termasuk penurunan emisi CO₂ industri hilir minyak dan gas bumi. Tetapi, dibandingkan dengan kredit karbon internasional, kelayakan biaya penurunan CO₂ di daratan sangat tergantung kepada jarak transportasi CO₂ melalui pipa.

Kata Kunci: penyerapan CO₂, hidrat CO₂, gas rumah kaca, penyerapan dan penyimpanan karbon.

ABSTRACT

Carbon Capture and Sequestration (Or Storage)—known as CCS needs to be implemented in various development activities in Indonesia including downstream oil and gas industry because the government of Indonesia has adopted the Paris Agreement on Greenhouse Gas Emissions Reduction. Various capture techniques have been developed for capturing CO₂ from post combustion emission. One of the new approaches considered for capturing CO₂ and hence reducing to atmospheric emissions is based on gas hydrate (crystallization) technology. The basis of the technology is the selective partition of the target component between the hydrate phase and the gaseous phase. It is expected that CO₂ is preferentially trapped and engaged into the hydrate crystal phase compared to the other components. Previous study found that

the gas/hydrate equilibrium pressure and temperature for the flue gas mixture in the range of 7.6 MPa and 11.0 MPa at 274 K and 277 K respectively, are inappropriate to the downstream oil and gas industrial reality because the operating cost will be expensive to compress the gas to the hydrate formation pressure. Suitable hydrate promoters including Tetrahydrofuran (THF) and Sodium Dodecyl Sulfate (SDS) can be used to achieve moderate hydrate formation pressure and energy consumption appropriate to the industrial reality. In the presence of THF and SDS about 62.3 Nm³/m³ CO₂ hydrate can be formed at 30 bar pressure and 274 to 277 K temperature within around 15 minutes reaction time. Many experiments result indicates that continuous hydrates formation will be feasible for scale-up to industrial settings including downstream oil and gas industry emission reduction if the technology assures an optimal contact between gas and liquid phases plus the proper hydrate promoter. However, compared to current international carbon credit, the feasibility of onshore CO₂ abatement cost in downstream oil and gas industry sensitively depends on the distance of CO₂ hydrate pipeline transportation.

Keywords: CO₂ capture, CO₂ hydrate, GHG, CCS.

I. INTRODUCTION

Carbon Capture and Sequestration (Or Storage)—known as CCS needs to be implemented in various development activities in Indonesia including downstream oil and gas industry because the government of Indonesia has adopted the Paris Agreement on Greenhouse Gas Emissions Reduction.

CCS has attracted interest as a measure for mitigating global climate change because large amounts of CO₂ emitted from fossil fuel utilization are potentially available to be captured and stored or prevented to release to the atmosphere. Various capture techniques have been developed for removing or isolating CO₂ from a gaseous stream. These techniques include absorption, adsorption, membrane separation and cryogenic fractionation. Having been separated the captured CO₂ emits from pre and/or post combustion must be definitely stored or used accordingly (Castellani et al. 2013).

One of the new approaches considered for capturing CO₂ and hence reducing to atmospheric emissions is based on gas hydrate (crystallization) technology. Gas hydrates have a large capacity for the storage of gases including CO₂. The basis of the technology is the selective partition of the target component between the hydrate phase and the gaseous phase. It is expected that CO₂ is preferentially trapped and engaged into the hydrate crystal phase compared to the other components.

Carbon dioxide gas hydrate (CO₂ n H₂O) is a nonstoichiometric clathrate compound which can be formed under proper temperature and pressure condition. The process of hydrate formation is a slowly crystallized procedure characterized with long induction time, large supercooled degree, and slow growth. However, to successfully make use of cool storage technic for CCS purposes with carbon dioxide gas hydrate, it must be formed fast and

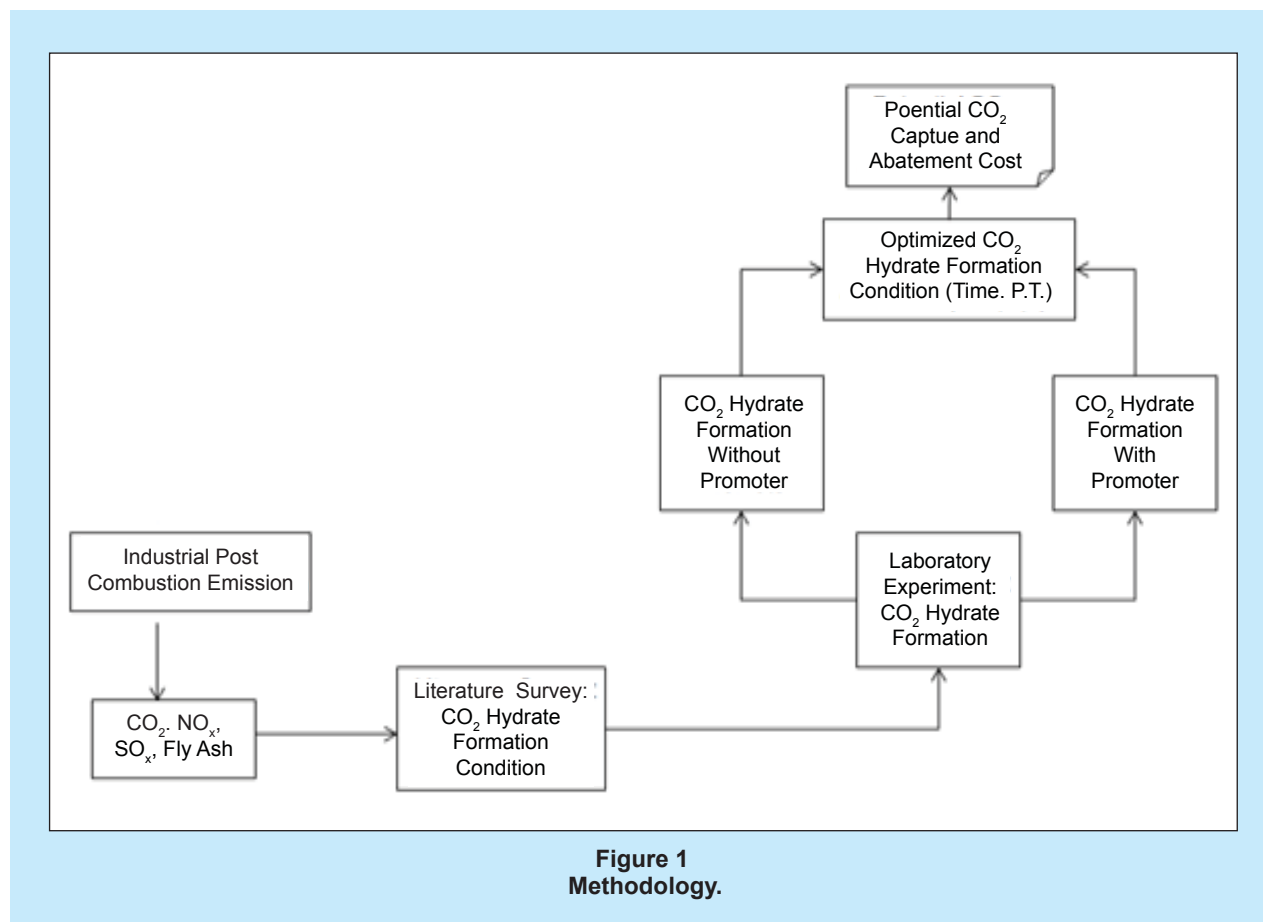
uniformly to get a high density of cool storage and easy to be handled. Currently, the common ways to improve gas hydrate formation are stirring, additive adding and making use of ultrasonic and magnetic field, and so on.

In this paper, laboratory experiment reports on CO₂ hydrates formation technology with and without a hydrate promoter are comparatively investigated. Moreover, the effect of impurities including fly ash/particulate matter, NO_x and SO_x on CO₂ hydrates formation are also discussed. Using necessary parameters, the technique is then conceptually applied to engage CO₂ release to atmosphere from downstream oil and gas post combustion plants.

II. METHODOLOGY

Steps conducted in this study is shown in Figure 1. Based on the technical guidelines for Indonesia's Green House Gas Emissions Reduction (Rencana Aksi Nasional Gas Rumah Kaca) documents, sectoral emissions are aggregated into three categories including energy, transport, industry (Daradjati 2012) in which industrial post combustion emission take places This paper focused on literature survey of hydrate formation experiments to find out a technique to capture post combustion emission gas from industry fuel utilization plant to cope with CO₂, NO_x, SO_x and fly ash.

A literature survey on CO₂ hydrate formation condition is carried out to identify pressure and temperature of the CO₂ hydrate formation covering the effects of additive and other components emitted on the condition. The lowest induction time, temperature, pressure and the amount of CO₂ hydrate formed at laboratory experiments is then selected. Potential CO₂ abatement cost is then calculated based on previous study on CO₂ hydrate onshore production plant.



III. RESULTS AND DISCUSSION

Around 15% to 20% mol of CO₂ and other components such as SO_x, NO_x and fly ash are emitted as flue gas from downstream oil and gas industry fuel utilization for power plants (and are released at atmospheric pressure (Castellani, et.al. 2013 and Kumar et al. 2013)). The gas/hydrate equilibrium pressure and temperature for the flue gas mixture is relatively high. For instance, the equilibrium pressures for the mixture containing 17.61% mol CO₂ are 7.6 MPa and 11.0 MPa at 274 K and 277 K, respectively. These conditions are inappropriate to the industrial reality, because the operating cost will be expensive to compress the gas to the hydrate formation pressure. Consequently, the main challenge is to obtain a lower operating pressure. This can be afforded by using specific compounds called promoters, which allow to reach moderate conditions for hydrate formation. Suitable promoter is essential to reduce the hydrate formation pressure and the energy consumption (Castellani et al. 2013 and Liu et al. 2008).

Usually, water-soluble additives are classified into kinetic or either thermodynamic additives.

Previous studies report a significant drop of hydrate equilibrium pressures at a particular temperature by adding small amounts of THF in the aqueous phase. It was found that hydrates formation pressure is considerably lower in the presence of the additive than compared to the case without the additive.

Various works reported that a small concentration of another surfactant promoter SDS, added to the aqueous phase drastically increased the kinetics of hydrate formation and showed that THF and SDS used in combination are efficient additives for promoting CO₂ hydrate formation.

Previous works on CO₂ hydrate formation experiment was carried out in moderate operating conditions, for the pressure values of 30 bar and temperature of 274 to 277 K. The maximum value of storage capacity was 62.3 Nm³/m³ in presence of THF and SDS with a reaction time of even 15 minutes with an improvements on reactor design allowed to overcome issues relating to thermal effects and mass transfer barriers. (Castellani et al. 2013 and Liu et al. 2008).

It has been reported that the use of 1 mol % of THF, as a thermodynamic promoter and SDS

Table 1
CO₂ hydrate capture cost estimation.

Capital Expenditure	: 9.5	million USD/year
Operating Expenditure	: 12.8	million USD/year
Lifetime	: 20	years
CO ₂ Capture Capacity	: 20,000	tonne/day
CO ₂ Capture Cost	: 4.76	USD/tonne
CO ₂ Pipeline Transportation Cost	: 0.0205	USD/tonne/miles

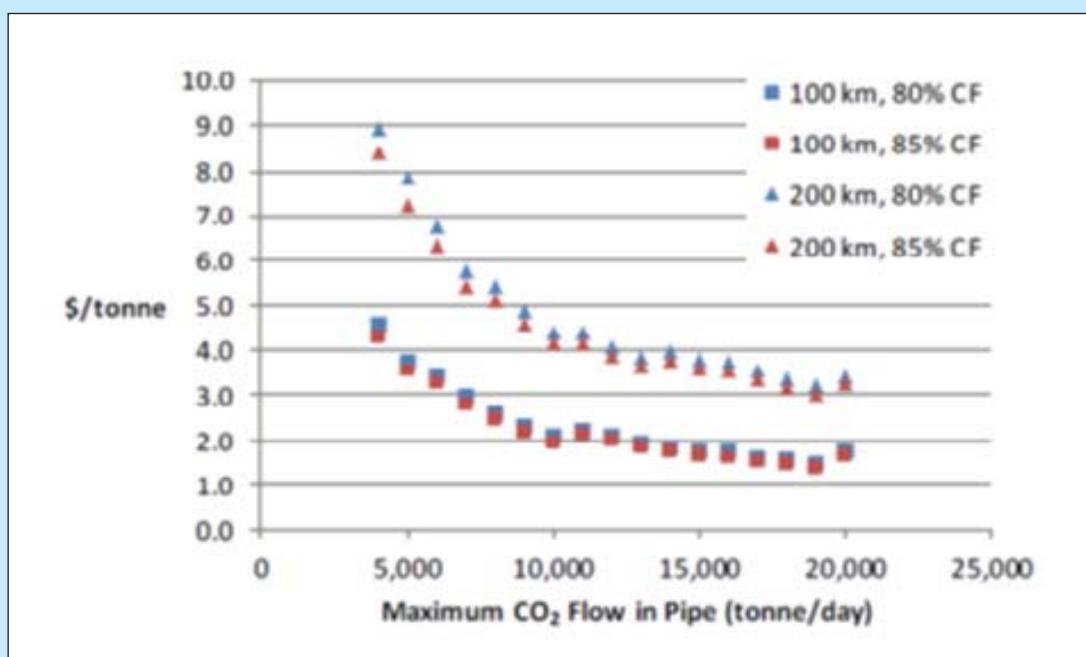


Figure 2
CO₂ hydrate pipeline transportation cost.

as kinetic promoters in the the fly ash contained Hydrate-Based Gas Separation (HBGS) process reduced the operating pressure significantly and found to improve the rate of hydrate formation. It was observed that the presence of fly ash rised the separation efficiency of the the HBGS process by reducing the induction time and increasing the kinetics of hydrate formation (Kumar et al. 2013 and Liu et al. 2008).

Post combustion CO₂ capture involves the separation of CO₂ from the flue gas mixture. Along with gases like carbon dioxide (CO₂), nitrogen oxides (NO_x), and sulfur oxides (SO_x), fly ash as particulate matter are generated by coal-based thermal power plants. However, concerns have been brought about that the application of CO₂ capture technologies might interfere with the current SO_x, NO_x, and fly ash removal technologies. Large-scale implementation of carbon capture will not be feasible

if the technology cannot withstand minor loads of fly ash and other acidic gases in the flue gas stream.

Kumar's study (Kumar et al. 2013) showed that the presence of 0.25 wt % fly ash impurity has no negative impact on the thermodynamics and kinetics of CO₂ hydrate formation, as flue gas from coal-based thermal power stations with a significant loading of fly ash can be efficiently used for CO₂ capture in the HBGS process. The study found that the presence of fly ash enhances the separation factor even in the presence of 1 mol % THF, the occupancy of carbon dioxide in the hydrate cages is significantly higher (11–17 times) than that of N₂.

Chen observed (Chen et al. 2014) the effects of SO₂ concentration and Tetra-n-Butyl Ammonium Bromide (TBAB) additive on the hydrate phase equilibrium. For the flue gas and SO₂ aqueous solution, the presence of SO₂ reduces the hydrate formation pressure. The higher the SO₂ concentration in aqueous solution, the easier the hydrate formed, and the higher the SO₂ concentration in equilibrium gas phase the higher the N₂ mole fractions in equilibrium gas phase compared to the feed flue gas, while CO₂ is lower due to its relative high solubility. For the experiment condition, the equilibrium pressure of hydrates formation increased in line with the rise of its temperature. Both SO₂ and N₂ mole fractions in equilibrium gas phase decreased whilst the CO₂ mole fraction increased because of the increased of the pressure. TBAB solution is not only reduces the equilibrium hydrates formation pressure markedly, but also helps the dissolution of SO₂ in aqueous solution. The SO₂ concentrations in equilibrium gas phase for the TBAB addition system are much smaller than those without TBAB addition. The pressure reducing effect of the TBAB promoter for SO₂ containing flue gas is dependent on the SO₂ concentration and smaller than that for flue gas without SO₂. A small amount of SO₂ resulted a synergy with TBAB to promote the hydrate formation, but the higher SO₂ concentration inhibited the hydrate formation, and caused the increase of hydrate formation pressure. The optimum SO₂ mass fraction in solution should be equal to or less than 0.010.

Many experiments result indicates that continuous hydrates formation will be feasible for scale-up to industrial settings including power plant emission reduction if the technology assures an optimal contact between gas and liquid phases plus the proper hydrate promoter. (Castellani et al. 2013 and Liu et al. 2008).

Since the existing downstream oil and gas industry fuel utilization plants are installed at various land in Indonesia, it is therefore necessary to identify previous works on onshore CO₂ hydrate capture cost estimation. Taken into account cumulative rate of inflation, CO₂ hydrate Capture Cost shown in Table 1 is calculated based on Aker Kvaerner Technology previous study report on CO₂ hydrate production plant in 2004 (Aker Kvaerner Technology 2004). Whilst CO₂ hydrate Pipeline Transportation Cost is derived from National Energy Technology Laboratory US Department of Energy study in 2014 (US Department of Energy, 2014) such as shown in Figure 2.

Figure 2 indicates that for particular CO₂ hydrate capture capacity, with regard to current international carbon credit, the feasibility of CO₂ abatement cost depends on the distance of CO₂ pipeline transportation. For example, if the current international carbon credit is USD 8/tonne, the 20,000 tonne/day CO₂ capture capacity will be feasible for the pipeline transportation less than 100 mile in distance.

IV. CONCLUSIONS

Considering preliminary literature survey of hydrate formation experiments to find out an option technique to capture post combustion emission gas from industry fuel utilization plant in Indonesia, the following points are concluded:

The gas/hydrate equilibrium pressure and temperature for the flue gas mixture in the range of 7.6 Mpa (76 bar) and 11.0 MPa (110 bar) at 274 K and 277 K respectively, are inappropriate to the industrial reality because the operating cost will be expensive to compress the gas to the hydrate formation pressure. In the presence of hydrate promoters such as THF and SDS, about 62.3 Nm³/m³ CO₂ hydrate can be formed at 30 bar pressure and 274 to 277 K temperature within around 15 minutes reaction time. Large-scale implementation of CO₂ hydrated capture will not be feasible if the technology cannot withstand minor loads of fly ash and other acidic gases in the flue gas stream. The presence of fly ash from flue gas mixture has rised the separation efficiency of Hydrate-Based Gas Separation process by reducing the induction time and increasing the kinetics of hydrate formation. The optimum SO₂ mass fraction of 0.010 in solution with TBAB has promoted the hydrate formation. With regard to current international carbon credit, the feasibility of

onshore CO₂ abatement cost sensitively depends on the distance of CO₂ pipeline transportation.

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