Modelling and process analysis of hybrid hydration–absorption column for ethylene recovery from refinery dry gas

Xiaobo Luo [a], Meihong Wang [a,*], Xingang Li [b,c,*], You Li [b], Chao Chen [b], Hong Sui [b,c]

[a] Process and Energy Systems Engineering Group, School of Engineering, University of Hull, HU6 7RX, UK
[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[c] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

HIGHLIGHTS

- Ethylene recovery from refinery dry gas using a novel hybrid hydration–absorption (HHA) process.
- Plate type column to be the physical base of HHA column model.
- First principle steady state model of HHA column.
- Vapour–liquid–water–hydrate (V–L–W–H) four phases involved in the system.
- Three case studies for different C_2H_4 concentrations in gas feed, L/G ratios and temperature profiles.

ARTICLE INFO

ABSTRACT

Effective recovery of ethylene from dry gas plays an increasingly important role to improve economic performance of refineries. Conventional approaches such as cryogenic separation and cold oil absorption are energy consuming. Hybrid hydration–absorption (HHA) process may be an effective way as hydrate formation takes place at temperature near the icing point. This paper aims to study the HHA column, which is the heart of the HHA process, through modelling and process analysis. A detailed steady state model was developed in gPROMS® for this vapour–liquid–water–hydrate (V–L–W–H) four phases system. A base case was analysed with real industry data as inputs. The composition distribution profiles inside the column were explored and the key parameters related with kinetics-controlled hydration process were investigated. Three case studies were carried out for different C_2H_4 concentrations in gas feed, L/G ratios and temperature profiles respectively. The results show (a) the separation performance of CH_4 and C_2H_4 in the HHA process remains significant for big range of C_2H_4 feed concentration; (b) L/G ratio has a great impact for hydrate formation and the separation performance of CH_4 and C_2H_4 improves when L/G ratio increases until reaching an optimal point; and (c) a cooling system is required to draw out the heat generated inside the HHA column so that the operating temperature of each plate can be at the temperature near the icing point to retain hydrate formation. This study indicates that the HHA process may be a more promising approach to recover ethylene from refinery dry gas in future industry application.

1. Introduction

1.1. Background

Ethylene is an important basic raw material in petrochemical industry. Oil refineries produce a large amount of dry gas with high ethylene content, such as delay coking gas and fluid catalytic cracking (FCC) gas [1]. Thus recovery and reuse of ethylene from oil refinery dry gases are important to improve the plant economic profile especially in the case oil refineries produce more light olefins nowadays [2]. Refinery dry gases mainly contain typical low boiling gas mixtures such as CH_4, C_2H_4, C_2H_6, N_2, and H_2 [1]. The conventional technologies for separating this low boiling gas mixture are cryogenic separation and cold oil absorption. The separation process of this light gas mixture requires a huge amount of energy. For example, cryogenic distillation approach employs an energy consuming refrigeration process [3]. For oil absorption, large solvent cycle rate is required for high recovery rate, which

* Corresponding authors at: School of Engineering, University of Hull, HU6 7RX, UK (M. Wang), School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China (X. Li).
E-mail addresses: Meihong.Wang@hull.ac.uk (M. Wang), lxg@tju.edu.cn (X. Li).

Nomenclature

Capital letters

A	kinetic parameters for hydration
A'	Antoine constants for calculating standard fugacity
B'	Antoine constants for calculating standard fugacity
C'	Antoine constants for calculating standard fugacity
C	Langmuir constant
D	column diameter (m)
H	heat (J/s)
HG	total gas consumption for hydrate formation per stage (mol/s)
HY	total hydrate mole flow rate per stage (mol/s)
K	kinetic parameters for hydration
L	total liquid mole flow rate per stage (mol/s)
N	the number of total stages
P	pressure (Pa)
Q	total heat draw out per stage (J/s)
R	ideal gas constant
R_e	Reynolds number
R_{ec}	Reynolds number for starting turbulence
SP	slurry volume per stage (m^{-3})
T	Temperature (K)
V	total vapour mole flow rate per stage (mol/s)
W	total water mole flow rate per stage (mol/s)
X	Antoine constants for calculating the Langmuir constant
Y	Antoine constants for calculating the Langmuir constant
z	Antoine constants for calculating the Langmuir constant

Case letters

c	the number of total components
h	hydraulic head loss of sieve plate internal
m	component mole fraction in hydrate phase (mol/mol)
r	hydrate generation rate per stage ($Kmol/min/m^{-3}$)

Δt_j	slurry residence time per stage (min)
x	component mole fraction in vapour phase (mol/mol)
y	component mole fraction in liquid phase (mol/mol)
z	component mole fraction in water phase (mol/mol)

Latin

$\Delta \mu$	driving force for hydration (J/s)
θ	mole fraction in small cave
α	constant 0
λ_1	the number of small cave in hydrate
λ_2	the number of large cave in hydrate
ρ	density (kg/m^3)

Superscript

f	Flash
$*$	big cave in hydrate

Subscript

abs	absorption process
DC	plate downcomer
hyd	hydration process
HY	hydrate phase
i	component i in the mixture; $i = 1, \ldots, c$
j	number j stage; $j = 1, \ldots, N$
L	liquid phase
w	outlet wire of plate
r	hydraulic head loss for resistance on plate
t	total hydraulic head loss on plate
V	vapour phase
W	water phase
0	standard conditions

makes both larger size of equipment and high regeneration energy. Some other technologies such as solvent extraction, chemical absorption, pressure swing adsorption and membrane separation were also studied [3], but their industry application are not common.

A novel method is to use clathrate hydrate [4] to separate ethylene and ethane from refinery dry gas. An advantage of hydrate approach over cryogenic separation is that hydrate formation can take place at the temperature around the icing point, thus deep cooling could be avoided. However two disadvantages, slow hydration rate and agglomeration, were also observed, which make it hard to combine hydration process into continuous operation process. Recent studies found water-in-oil emulsion introduced into hydrate formation process could not only enhance the hydrate formation rate and improve single stage separation efficiency but also prevent the hydrate agglomeration [5]. With this finding, the process of combining the oil absorption process and hydration process [6] was designed to recover ethylene and ethane from oil refinery dry gas.

1.2. Previous researches

Gas hydrate (also known as clathrate hydrate) is water-based solids with physical properties resembling ice, in which small guest molecules, such as low molecular weight gases methane as well as some light hydrocarbons and freons, are trapped in cages of hydrogen bonded host water molecules [4]. Three types of hydrate structures have been determined: sI, sII, and sH depending upon the temperatures and pressures of formation processes and

the compositions if a gas mixture was involved [7]. Gas hydrate attracted the research intention as one of main problems in the gas transportation from 1934 [8]. Later wide distribution and huge capacity of natural gas hydrates are found in deep water all over the world, which could be a source of future fuel [9]. A novel application of gas hydrate is the separation of gas mixture [10], such as separation of C_2H_4 from $CH_4 + C_2H_4$ mixture and other components like CO_2, CH_4 and H_2S. By managing temperatures and pressures of hydrate formation processes, hydrate may exhibit different selectivity to different gas components in a gas mixture. Meanwhile, weak hydrogen bonds of hydrate are easy to be broken with a little energy requirement, which makes it easy to enrich objective gas and to circulate the solvent by regenerating the rich solvent.

Recent fundamental studies focus on the thermodynamics of hydrate and kinetics of its formation and dissociation. Van der Waals and Platteeuw [11] proposed a statistic thermodynamics model for the phase equilibrium in porous media, which was used with Gibbs–Thomson relationship to determine the interfacial tension between hydrate and water from experimental data. Later a thermodynamics model based on the concepts of reaction and adsorption two-step formation mechanism was reported by Chen and Guo [12,13]. The study of the kinetics of hydrate formation is hard because the process happens in pores are difficult to control and monitor [14]. Englezos et al. [15] observed that the formation rate is a strong function of the driving force and that formation occurs in both the interface and the liquid phase. The kinetic model proposed by Kashchiev and Firoozabadi [16] expresses the driving force is the supersaturation chemical potential difference, which depends on the actual gas concentration in the solution. Thus the