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Optimization of inhibition conditions of tetrahydrofuran hydrate formation via the fractional factorial design methodology

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ABSTRACT

In the present study, 2^{4-1} fractional factorial design has been used to optimize the inhibition conditions of tetrahydrofuran (THF) hydrate formation in the presence of acetone and L-leucine. The variables, L-leucine concentration (wt%), acetone content (v/v%), operating temperature and stirrer speed of reactor have been selected as the independent variables. This method has been designed to obtain significant effects on two responses variables, delay time and equilibrium temperature of THF hydrate formation, and 8 experimental runs have been carried out with two replications and four central points. The ANOVA results show that at the 95% confidence level the operating temperature and L-leucine concentration significantly affect the delay time and equilibrium temperature of hydrate formation, respectively. A first-order polynomial equation is developed to relate the responses and operational variables. The fitted model shows a good agreement between predicted and actual responses ($R^2 = 0.814$ and 0.823; mean deviation = ±3 and ±1%). The optimal process conditions were: L-leucine concentration of 1 wt%, acetone of 7.5 v/v% and operating temperature of −5 °C for both responses and stirrer speed of reactor of 5 rpm for response 1 and 7 rpm for response 2.

1. Introduction

Clathrate hydrates are inclusion compounds which guest molecules are trapped in water cavities composed of hydrogen-bonded water molecules. Typical guest molecules include methane, ethane, carbon dioxide and some refrigerants that are stabilized in the cavities of sI, sII and sH hydrate via van der Waals interaction forces at conditions of low temperature and/or high pressure (Carroll, 2002; Mohebbi and Behbahani, 2014; Sloan, 2003; Sun et al., 2011; Vysniauskus and Bishnoi, 1983). The conditions of hydrate formation are common in oil and gas transmission, therefore, hydrate formation is a major possible reason of pipeline blockage and many researches have been also performed to prevent hydrate formation (Kelland, 2011; Keshavarz Moraveji, 2012).

Since prediction of the temperature and pressure under which gas hydrates form is important, Ghayyem et al. (2014) represented the correlation to predict their formation temperature. The new proposed correlation has shown the most accurate one among all the available correlations.

Currently, the suitable way of preventing hydrate blockages is to use chemical inhibitors. These may act by shifting the water/hydrocarbon/hydrate 3 phase equilibrium line, such as methanol or glycols, or delay the onset of nucleation and crystals growth like polyvinylpyrrolidone (PVP) or polyvinylcaprolactam (PVCap) (Niang et al., 2010; Storr et al., 2004; Tang et al., 2010; Valberg, 2006). Many studies have been also conducted to optimize the hydrate formation inhibition conditions. Talaghat (2014) studied the enhancement of the performance of modified starch as a kinetic inhibitor in the presence of polyoxides such as ethylene oxide (PEO) and polypropylene oxide (PPO) for simple gas hydrate formation in a flow mini-loop apparatus. Pal and Kundu (2013) performed studies based on density functional theory to elucidate the role of methanol as a methane hydrate inhibitor and optimized a methane hydrate pentagonal dodecahedron cage's geometry. They found that methanol destabilizes the mentioned geometry of methane cage. Riazi et al. (2014) firstly studied hydrate formation conditions for methane and pure water system and then imposed corrections on this system correlation to predict the formation conditions for natural gas and in the presence of impurities and salts. They developed a correlation using Matlab curve fitting software and then optimized using methods like Genetic Algorithm. Paez et al. (2001) provided a systematic approach in deploying low-dose inhibitors in existing facilities and new development for gas hydrate formation processes. They found that once a LDI is deployed, a management system should be created to keep track of the performance of the treatment and help predict situations where gas

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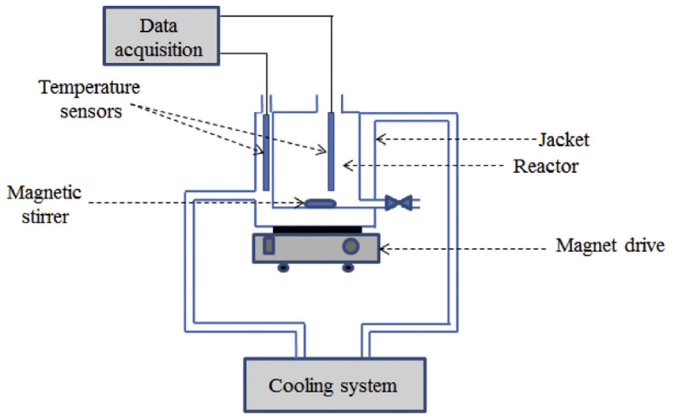

Fig. 1. Experimental setup.

Table 1
Experimental ranges and levels of the factors used in the design of experiment.

Variable	Coded symbol	Values of coded levels		
		−1	0	+1
Operating temperature, °C	A	−7	−6	−5
L-leucine concentration, wt%	B	0.5	0.7	1
Acetone, in volume ratio of the solution	C	7.5	8.5	10
Stirrer speed rate of reactor, rpm	D	5	6	7

hydrates may form and optimize this performance whenever possible.

In this work, the significant operational factors of THF (tetrahydrofuran) hydrate formation inhibition by L-leucine and acetone have been studied. It has been previously reported that the molecules such as furan, THF and 1,4-dioxane are non-gaseous hydrate former and they can form sII hydrate under atmospheric pressure as suitable alternative molecules for gas hydrates. They can be used as an analog to study the gas hydrates without the requirement of high pressures (Dirdal et al., 2012; Karamoddin and Varaminian, 2013, 2014; Naeiji et al., 2014). L-leucine is a natural hydrophobic amino acid that has been previously studied as KHIs (kinetics hydrate inhibitors) for CO_2 hydrate inhibition (Sa et al., 2013). It is environmentally friendly KHIs with enhanced biodegradability. Acetone is the simplest ketone with the formula $(CH_3)_2CO$. It is miscible with water and it can affect hydrate formation as an inhibitor or a promoter depending on its concentration in solution (Javanmardi et al., 2004; Kamran-Pirzaman et al., 2013). Hereby, THF has been selected to form sII hydrate formation under atmospheric pressure and a molar ratio of 1:17 (THF-water) and acetone and L-leucine have been chosen as inhibitors in this paper. The main objectives were to determine the delay time and the equilibrium temperature of hydrate formation. The experimental data have been generated by a 2^{4-1} fractional factorial design of experiments with two replications and four central points. A regression model has been represented for each response and optimization of the

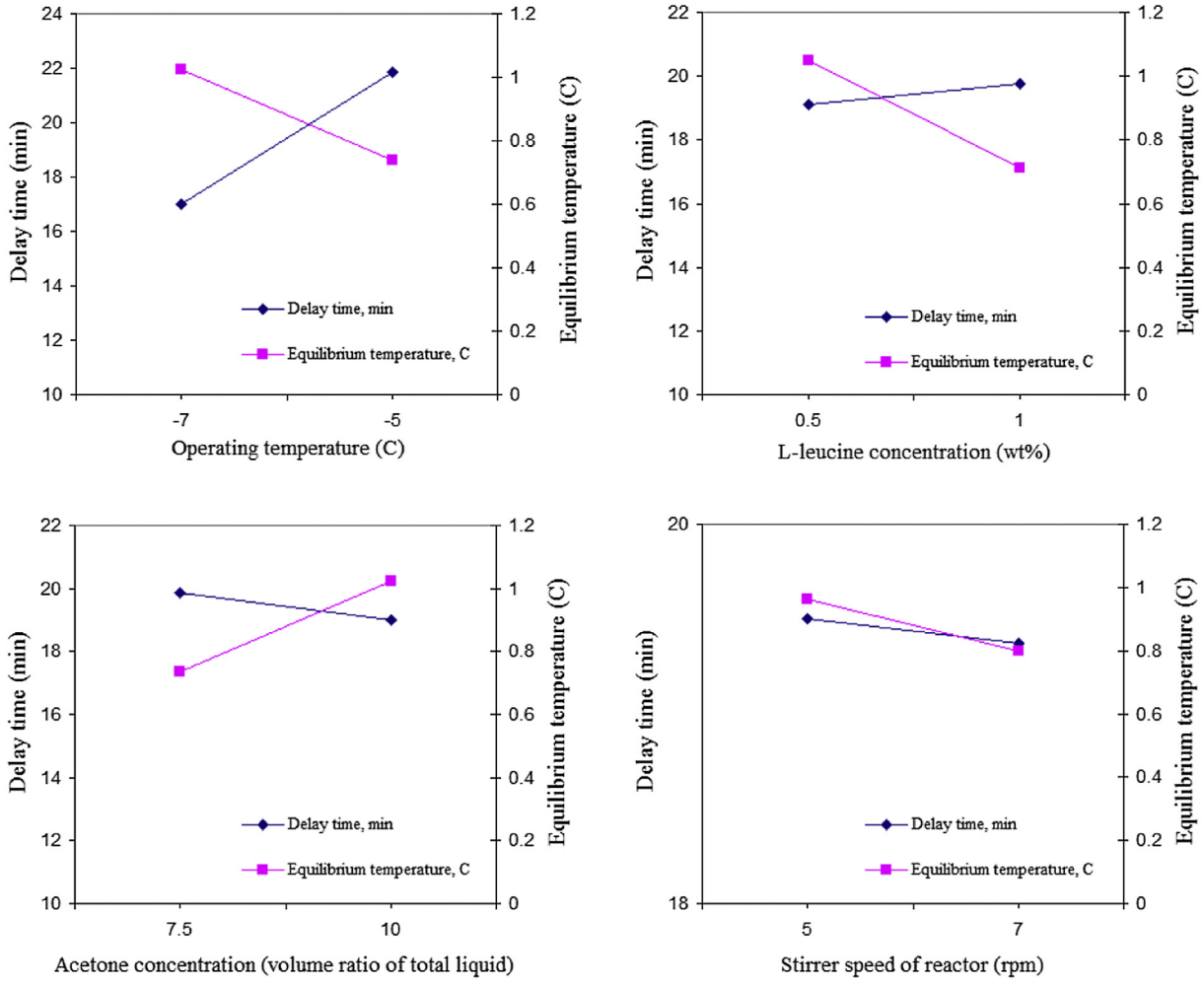

Fig. 2. Effect of four process parameters on delay time and equilibrium temperature of THF hydrate formation.