

Optimal Operation of the Cyclic Claus Process

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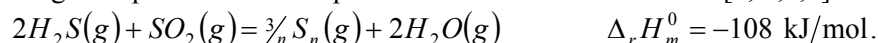
Abstract

The dynamic analysis and optimization of the novel cyclic Claus process, a four-step, one-bed, vacuum swing adsorptive reactor (VSAR) is studied. The partial differential and algebraic equations describing the physical behavior of the system are stated in a dimensionless form. The model equations are solved using gPROMS®, and a NLP problem is formulated to maximize a performance objective function. A rSQP based optimization is used to search for the optimum operating parameters. Since the reactant feed time is an important factor for the efficiency of a cyclic process, our work in this study focuses on attaining maximum reactants feeding time at high conversion, exploring the optimal design and operating parameters for the reactor.

Keywords Adsorptive reactor, cyclic Claus process, vacuum swing adsorptive reactor, process optimization, adsorbent/catalyst distribution strategy.

1. Introduction and background

The cyclic Claus process is a novel process that combines the reaction of hydrogen sulfide with sulfur dioxide and the adsorption of water vapor in an adsorptive reactor to maximize conversion and to reduce down stream gas impurities. A γ -Alumina oxide catalyst and a 3A zeolite adsorbent for the selective removal of water from the reaction zone are used in the novel integrated process for the equilibrium limited Claus reaction [1,2,3,4]:



The major advantages of this novel process are reduced capital and operating costs and increased energy efficiency due to the elimination of inter-stage coolers and separators. In addition, the conversion of the exothermic equilibrium limited Claus reaction is enhanced by affecting the kinetics and thermodynamics of the reaction system via the manipulation of the concentration profile of the by-product water. The multifunctional reactor concept for the Claus process was proposed by Agar [1]. His research group [2,3,4,5] conducted experimental work to assess the feasibility of the developed process and proposed general guidelines for the distribution of the catalyst to adsorbent ratio on the reactor level. Desorption was not considered in these studies. Xiu, Li, and Rodrigues [6] developed a new generalized strategy for adsorptive reactor performance enhancement by controlling the subsection wall temperatures. In this paper, a four-step one-bed dimensionless model of a vacuum swing adsorptive reactor (VSAR) is presented for the novel cyclic Claus process. A systematic strategy is used for the optimization of this novel Claus process taking into consideration the main variables that affect the design and the operation of the vacuum swing adsorptive reactor. An overall NLP formulation of the optimization problem of the operating and design parameters to maximize the column production rate is formulated and solved. As the solution of nonlinear, non-convex problems, may depend on the starting point, and convergence may be difficult to establish, a two level approach was chosen. First conversion and feeding time were maximized for subsets of the overall degrees of freedom. The solution obtained was used to initialise the solution of the full problem.

2. Mathematical development

A standard Skarstrom 4-step, one-bed, VSAR cycle consists of: pressurization, feed, evacuation and purge-evacuation are proposed for the novel cyclic Claus process. The parabolic system of equations describing the physical behavior are normalized and the following model results. Components mass balance:

$$\frac{\partial(y_i P)}{\partial \tau} = \frac{D_{ax} t_s}{L^2} \frac{\partial^2(y_i P)}{\partial x^2} - \frac{u_0 t_s}{L} \frac{\partial(y_i P U)}{\partial x} + F(1-\varphi) \frac{\rho_c t_s}{c_0} v_i^r R_{xn} + F\varphi v_i^{ad} \frac{\partial Q}{\partial \tau}$$

Total mass balance:

$$\frac{\partial P}{\partial \tau} + F\varphi \frac{\partial Q}{\partial \tau} = -\frac{u_0 t_s}{L} \frac{\partial(UP)}{\partial x} + \sum v_i^r F(1-\varphi) \frac{\rho_c t_s}{c_0} R_{xn}$$

Reaction rate [3]:

$$R_{xn} = k_1 p_0^{1.25} y_{H_2S} y_{SO_2}^{0.25} P^{1.25} - k_2 p_0 y_{H_2O} P$$

Adsorption kinetics (LDF model) [3]:

$$\frac{\partial Q}{\partial \tau} = 60D_0 t_s / d_p^2 (1 / (1 + (0.75a / (\epsilon_p c_0^{0.75}))) / (y_{H_2O}^{0.25} P^{0.25}))) ((a / c_0^{0.25}) y_{H_2O}^{0.75} P^{0.75} - Q)$$

Momentum equation:

$$-\frac{\partial P}{\partial x} = \frac{180 \mu u_0 (1 - \epsilon)^2 L}{\epsilon^3 d_p^2 p_0} U$$

Performance indices:

$$\text{Conversion} = (\text{Feed of } H_2S - \text{Effluent of } H_2S) (\text{mol/s}) / \text{Feed of } H_2S (\text{mol/s})$$

$$\text{Flux}_i = \frac{t_2}{t_{\text{cyc}}} \int_{\tau_1}^{\tau_2} (y_i P U)_{x=1} d\tau ; \quad \text{Pr} = c_0 u_0 A \sum_{i=1}^{nc} \text{Flux}_i$$

$$Y_{\text{impurity}} = \frac{(\text{Effluent of } H_2S + \text{Effluent of } SO_2)_{x=1} (\text{mol/s})}{(\text{Effluent of } S + \text{Effluent of } H_2S + \text{Effluent of } SO_2)_{x=1} (\text{mol/s})}$$

Table 1 shows the system boundary conditions. Simulation data is given in [2,3]
Table 1. Boundary conditions for different steps

	$x = 0$	$x = 1$
Pressurization	$y_i = y_{if}, P = P_f$	$\partial y_i / \partial x = 0, U = 0$
Feed	$y_i = y_{if}, UP = U_{fstart} P_f$	$\partial y_i / \partial x = 0, P = P_f$
Evacuation	$\partial y_i / \partial x = 0, P = P_v$	$\partial y_i / \partial x = 0, U = 0$
Purge	$\partial y_i / \partial x = 0, P = P_v$	$y_i = 0, UP = U_{pstart} P_v$

where: y_i : molefraction of component i ; u_0 : reference velocity (0.1 m/s); p_0 : reference pressure (101325 Pa); T_f : bed feed temperature (523 K); t_s : cycle step time (s); Q : normal. solid concentration; P : normal. pressure; U : normal. velocity; τ : normal. time; x : normal. Length, F : phase ratio $((1-\epsilon)/\epsilon$, with ϵ being column porosity); U_{fstart} , U_{pstart} : normal. interstitial velocities of feed and purge steps; P_v : normal. vacuum pressure; P_f : normal. feed pressure; A : area (m^2).

The model equations were discretized using orthogonal collocation on finite elements (OCFEM, 3, 20) and a BDF method with variable step size for spatial and temporal discretisation. At the cyclic steady state (CSS), the process states at the start and at the end of the cycle are identical. The mass balance at the CSS was considered as an indication of the numerical accuracy and as a constraint for verification of the cyclic steady state in optimization.

3. Formulation of the optimization problem

The effective cleaning of the adsorbent plays a major role in enhancing conversion and producing high purity product. If the adsorbent regeneration is not complete, it affects the production during the next step. The bed is periodically desorbed using inert gas N_2 at low pressure. The cycle time, the velocities of the feed and purge steps, the purge pressure, the operating temperature and the distribution of the adsorbent and catalyst are the operating and design parameters that affect the performance of the adsorptive reactor. These degrees of freedom were included in an NLP optimization problem to maximize the conversion and to determine the optimal operation of the VSAR for the cases of uniform and non-uniform adsorbent distribution. The results are shown in table 2.

$$\text{Max}_K(\text{Conversion})$$

s.t.

$$Y_{\text{impurity}} \leq Y_{\text{impurity}_{\text{max}}} ; \quad mb_{\text{css}} \leq \varepsilon_{\text{css}} ; \quad t_{\text{css}} \leq t_{\text{horizon}} \leq t_{\text{final}} ; \quad K^{\text{min}} \leq K \leq K^{\text{max}}$$

$$\text{where; } K_{\text{non-uniform}} \equiv \{l_1, l_2, l_3, \varphi_1, \varphi_2, \varphi_3, T_f, P_v, t_1, t_2, t_3, t_4, u_{f\text{start}}, u_{p\text{start}}\}$$

$$K_{\text{uniform}} \equiv \{\varphi, T_f, P_v, t_1, t_2, t_3, t_4, u_{f\text{start}}, u_{p\text{start}}\}$$

where: t_{css} : cyclic steady state simulation time (s); mb_{css} : relative mass balance error; P_r : production rate [mol/s]; $\varphi_1, \varphi_2, \varphi_3$: adsorbent volume fraction in each zone; l_1, l_2, l_3 : bed reaction and equilibrium zones lengths; ε_{css} : 0.007; $Flux_i$: normalized output fluxes at the feed step; Y_{impurity} : average impurity dry basis; nc: number of components excluding inert; K : vector of decision variables.

Table 2. Optimization results for different solid distributions

Decision vars	t_1	t_2	t_3	t_4	T_f	P_v	$U_{f\text{start}}$	$U_{p\text{start}}$
Nonuniform	2.238	998.558	2.0	1000.42	530.742	0.382	1.368	4.754
Uniform	2.093	995.475	2.0	1000.93	525.564	0.365	1.370	4.662
Bounds	Min	2	600	2	600	500	0.01	1.0
	Max	100	2000	100	2000	573	0.50	4.0
Decision vars	φ	φ_1	φ_2	φ_3	l_1	l_2	l_3	
Nonuniform	-	0.632	0.686	0.227	0.201	0.220	0.179	
Uniform	0.484	-	-	-	-	-	-	
Bounds	Min	0.1	0.1	0.1	0.1	0.1	0.1	
	Max	0.9	0.9	0.9	0.9	0.4	0.4	0.4
Max conversion	Nonuniform = 99.97				Uniform = 99.95			

The optimum parameters result in a high conversion and a cleaned bed. It is clear that both distributions can provide high conversion. In addition, the three

bed zones had shown that the two first zones have similar solids distributions while the rear zone has a higher value of catalyst volume fraction what can be explained by a further improvement of the removal of traces in this zone. Since the reactant feed time is an important factor for the efficiency of a cyclic process, a long reactant feeding time is the major goal of process optimization. In addition, conversion of at least 99.5% is vital in this process. The effect of the feeding time on the production rate was studied. The optimum feeding time was computed assuming that all other variables are kept at their previously computed optimal values for each case.

$$\text{Max}_{t_2} (\text{Pr})$$

$$\text{s.t. } \text{conversion} \geq \text{conversion}_{\min} ; \quad mb_{css} \leq \varepsilon_{css} ; \quad t_{css} \leq t_{horizon} \leq t_{final}$$

Table 3. Attaining maximum feeding time in each distribution strategy

Solid distribution	Dec. var.	Optimum	Objective function	Base case	Bounds	
Non uniform	t_2	1741.62	0.00014 [mole/s]	0.000084	998	2000
Uniform		1636.02	0.00012 [mole/s]	[mole/s]	995	2000

As can be seen from table 3, due to the different mechanisms of reaction and adsorption, the catalyst and the adsorbent should not be equally distributed in the bed in order to provide operating conditions that lead to an efficient utilization of both functionalities. An optimal operation of a cyclic adsorptive reactor that combines high productivity, high conversion and maximum feeding time should take into consideration all the operating and design parameters. The optimization degrees of freedom include the lengths of the bed zones, the solid ratios in each bed zone, the durations of each step, feed and purge velocities, purge pressure, and feed temperature. These parameters were considered for optimization with the objective of maximizing the bed production rate while maintaining the high conversion. Mathematically:

$$\text{Max}_{\mathbf{K}} (\text{Pr})$$

s.t.

$$\text{conversion} \geq \text{conversion}_{\min} ; \quad mb_{css} \leq \varepsilon_{css} ; \quad t_{css} \leq t_{horizon} \leq t_{final} ; \quad L = L_{bed}$$

$$\mathbf{K}^{\min} \leq \mathbf{K} \leq \mathbf{K}^{\max} ; \quad \mathbf{K} \equiv \{l_1, l_2, l_3, \varphi_1, \varphi_2, \varphi_3, T_f, P_v, t_1, t_2, t_3, t_4, u_{fstart}, u_{pstart}\}$$

The equations were formulated in the gPROMS (v-3.01) language and the reduced successive quadratic programming algorithm (rSQP) implemented in gOPT was used [7]. The optimum values were obtained after 11 NLP iterations and 13 NLP line search steps, and it took a total CPU time of 77945.5 seconds. It is obvious from the results (Table 4) that the use of different adsorbent

volume fractions and the tuning of the bed lengths results in improved adsorptive reactor performance with respect to the feeding time. The cycle times, t_2 , t_4 result in a design that enables the continuous operation of a reactor with two beds.

Table 4. Optimization of production rate maximization

Decision var.	t_1	t_2	t_3	t_4	T_f	P_v	U_{fstart}	U_{pstart}
Optimum value	2.0	1296.22	2.0	1000	512.331	0.488	2.11	8.0
Bounds	Min	2	998	2	1000	500	1.0	1.0
	Max	100	2000	100	2000	573	4.0	8.0
Decision var.	φ_1	φ_2	φ_3	l_1	l_2	l_3	Objective Function	
Optimum value	0.548	0.862	0.10	0.199	0.209	0.192	Pr = 0.00019 [mole/s]	
Bounds	Min	0.1	0.1	0.1	0.1	0.1	0.1	
	Max	0.9	0.9	0.9	0.4	0.4	0.4	

4. Conclusions and future work

The optimum design of a novel cyclic Claus process vacuum swing adsorptive reactor has been presented. It was found that the adsorptive reactor can provide enhanced conversion by optimizing the adsorbent volume fraction in the bed. In addition, optimization of the operating and design parameters in cyclic adsorptive reactor process results in a high performance VSAR in terms of feeding time and production rate. The production rate can be increased by more than two times compared to the base case production rate. In comparison to previous work, in this work the bed reaction and equilibrium zones lengths, solid ratios and the operating parameters were included as decision variables in the optimization. The relative mass balance error and the cyclic steady state simulation time were implemented as constraints in the Picard iterations optimization. The column performance improvement is attributed to the choice of an operating window in which all parameters interact optimally. Future work will be to develop an efficient control strategy while maintaining maximum process efficiency.

References

1. D.W. Agar, *Chem. Eng. Sci.*, 54 (1999) 1299
2. M.P. Elsner, C. Dittrich, and D.W. Agar, *Chem. Eng. Sci.*, 57 (2002) 1607
3. M.P. Elsner, M. Menge, C. Müller, and D.W. Agar, *Catal. Today*, 79-80 (2003) 487
4. M.P. Elsner, Ph.D. Dissertation, University of Dortmund, (2004)
5. P.S. Lawrence, M. Gruenewald, W. Dietrich and D.W. Agar, *Ind. Eng. Chem. Res.*, 44 (2005).
6. G.h. Xiu, P. Li and A.E. Rodrigues, *Chem. Eng. Sci.*, 58 (2003) 3425
7. M. Oh, and C.C. Pantelides, *Comput. Chem. Engng.*, 20 (1996) 611