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Conceptual Design of the Eastman Organic Wastewater Treatment Process

Wende Tian[a,*], Zhe Cui[a], Hua Qin[b], Lening Li[a]

[a]College of Chemical Engineering, Qingdao University of Science & Technology, 266042 Qingdao, China
[b]Blue Diamond International Co., Ltd, 100016 Beijing, China
tianwd@qust.edu.cn

The organic wastewater produced in Eastman process is composed of a large quantity of organics with approximate 60,000 mg/L of chemical oxygen demand (COD). With a flow rate of about 1,011 kg/h, this organic rich wastewater will contaminate environment heavily if discharged without any treatment. This paper developed one “waste control by waste” scheme to treat this wastewater by simulation and experiment approaches. First, extraction equilibrium and reaction kinetics of TXIB are investigated through experiments with key parameters estimated. Second, an extraction scheme using an own synthesized ester (2,2,4-trimethyl-1,3-pentanediol- di-isobutyrate, TXIB) as extractant is selected since it can avoid the solvent recovery problem. The scheme is simulated and evaluated with ASPEN PLUS software. Finally, the optimum designing scheme of Eastman wastewater treatment process is determined with necessary parameters obtained from the experiment. A plantwide control structure is also developed, and its effectiveness in the face of large disturbances is demonstrated by dynamic simulation.

1. Introduction

With the rapid development of industrial processes, iindustrial wastewater is the main source of the environmental pollution (Rashidi et al. 2015), so its disposal has become the emphasis of wastewater treatment (Pang et al., 2011). Organic wastewater treatment methods proposed in the literature can be classified as biological degradation method and physical-chemical method respectively (Estrada et al., 2015). As a physical-chemical method, solvent extraction method receives more and more attentions in industry fields like petrochemical (Hu et al., 2015), hydrometallurgy (Kul et al., 2015), graphic industry (Monteiro et al. 2013), etc. The main disadvantage of solvent extraction method is the loss of solvent and the caused secondary pollution. Accordingly, some improvements have been made to increase extraction efficiency (Ben Fredj et al,. 2015). The extraction and back-extraction of pesticides from aqueous solutions using ionic liquids were studied and intensified in CPE (Centrifugal Partition Extraction) device (De Gaetano et al., 2016). The extraction performances in a multi-stage rotating disc contactor were compared in both batch and continuous cloud point extraction fashions for the removal of organic solutes from wastewater (Taechangam et al., 2008).
This paper focuses on the wastewater treatment problem of Eastman production of 2,2,4-trimethyl-1,3-pentanediol (TMPD) handled by solvent extraction method. In wastewater treatment domain, some design works have been performed in recent years from viewpoint of retrofitting and sustainabilityy (Gai et al. 2015). Motivated by these efforts and based on our previous conceptual design work (Tian et al. 2009), this paper develops a "waste control by waste" scheme to dispose of the Eastman wastewater, in which the pentanediol and isobutyrate in the wastewater are reacted with each other to produce a special ester as the extractant (Babadagli et al., 2005).

2. Experiment

The experiment work for the proposed process is divided into two parts: extraction and reaction. This section demonstrates and discusses the results obtained by the experiments in order to use them to guide the simulation in the next section.

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2.1 Extraction experiment

TMPD wastewater is primarily composed of sodium isobutyrate (20.9 kg/h), TMPD (3.3 kg/h), isobutyric acid (1kg/h), isobutyraldehyde (6.7 kg/h), and water (1011 kg/h). It is difficult to empirically choose an appropriate extractant without numerous verifying experiments. Organic conception diagram, which uses organic value (O) and inorganic value (I) of compounds to represent their mutual solubility, has been widely used in organic chemistry and chromatography for solvent selection purposes. So in this paper, the extractant is selected by using organic conception diagram. The I and O values for each organic compound related to the wastewater are calculated, including TXIB (2,2,4-trimethyl-1,3-pentanediol di-isobutyrate) because it could be synthesized by isobutyric acid and TMPD. The O/I ratio value of TXIB is 1:1, and other compounds are all close to this value, so the similar O/I ratio values indicate that TXIB is mutually soluble with the organic ingredients in the wastewater. TXIB is therefore selected as the extractant. This extractant choice facilitates the utilization of waste compounds to make up for the extractant loss in multi-stage extraction process without secondary pollution.

Extraction effect of TXIB can be measured by distribution coefficient K_A as follows:

$$K_A = \frac{x_{AE}}{x_{AR}} \quad (1)$$

where x_{AE} denotes the fraction of solute in extraction phase, x_{AR} denotes the fraction of raffinate.

The experiment steps used to determine distribution coefficient are as follows:

(1) Accurately weigh a quantity of wastewater and ester, and then mix them evenly;

(2) Put the mixture in a separatory funnel for 2 hours until layering;

(3) Sampling from upper and lower liquid layer, and determine COD values with potassium dichromate method;

(4) Substitute COD values for the concentration in Eq(1) to calculate distribution coefficient.

Ten wastewater samples with a concentration of ten equal of C (original organic concentration in wastewater): 0.1C, 0.2C, 0.3C, ..., 1.0C are extracted with 1:5 ratio of extraction phase volume to material liquid volume. After COD assaying, the COD difference between extraction phase and untreated wastewater is calculated as COD of extraction phase, and the COD ratio of extraction phase to raffinate is calculated as overall distribution coefficient of the mixture. The square points in Figure 1 show the extraction results under room temperature. Figure 1 also shows the solid curve, which is fitted from COD data, rises rapidly at first and then smoothly with an increase of raffinate COD. Based on the COD values in Figure 1, distribution coefficient is obtained using the nonlinear least square method.

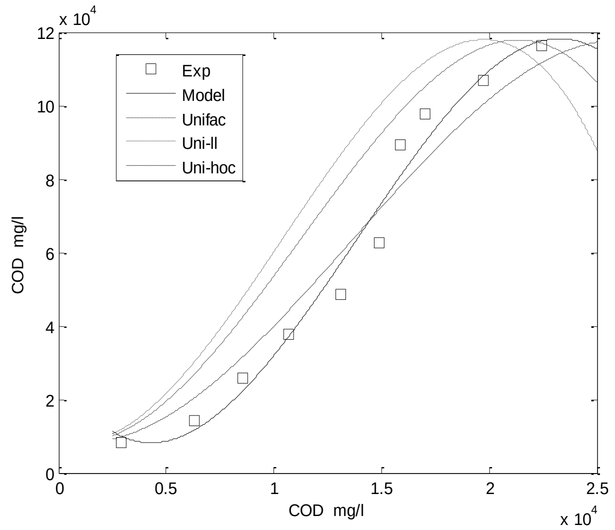

Figure 1: The equilibrium line of extraction

2.2 Esterification experiment
Esterification reaction Eq(2) is of great importance in this disposal process due to its supplement role for extractant. This reaction is controlled in a temperature range from 120 ℃to 140 ℃. Because there are many factors affecting the reaction, the orthogonal experiment is utilized to reduce experiment workload. Orthogonal experiment chooses L9 (3^4) table with fixed molar ratio of acid to alcohol as 2:1 and with esterification rate as the index of the investigation. The optimum reaction condition can be obtained from range analysis as follows: reaction temperature is 130 °C. reaction time 3.5 is hours, and catalyst content is 8%.

$$2C_4H_7COOH + C_8H_{18}O_2 \leftrightarrow C_{16}H_{30}O_4 + 2H_2O \qquad (2)$$

3. Process simulation

In our proposed disposal process, the wastewater is adjusted to pH=2 with sulfuric acid in a static mixer and then contacts with the extractant counter-currently in an extraction column to remove organics from wastewater. The raffinate (wastewater) in extraction column is discharged and the extraction phase is fed to an esterification reactor where TXIB is produced by reacting TMPD with isobutyric acid. The esterifier gas vent returns to static mixer after cooling and its liquid stream enters a distillation column. Distillation column produces isobutyraldehyde and unconverted isobutyric acid in the distillate and a recycle extractant stream of TXIB to the bottom of the extraction column. The system parameters of the simulation process are listed in Table 1. And the simulation diagram is shown in Figure 2.

Table 1: System Parameters

Name	Parameter Design
Physical Property Method	UNIFAC
Component Custom	Sodium Butyrate
Distillation Tower	Tray Number 10
Kinetic Parameters	k_0=4.08×10^{-3} l^2/(mol^2·min) E_a=5.73×10^3 kJ/kmol

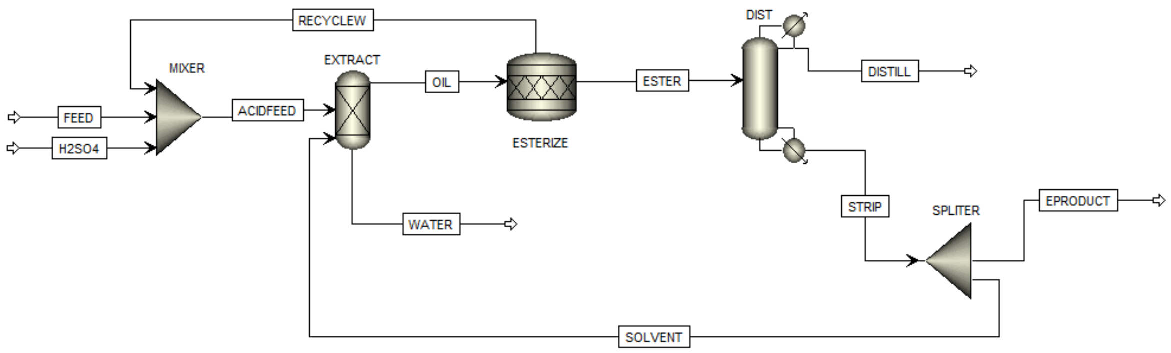

Figure 2: Simulation flowsheet of wastewater treatment in Aspen Plus 7.2 software

To decrease the energy consumption of distillation, the ester circulation flowrate is set as one-fifth of the aqueous phase of the extractor. Table 2 lists the simulation value of main streams.

4. Plant wide control

4.1 Dynamic simulation
To carry out the dynamic simulation, the dimension of devices should be specified, including the installation information (vertical height or horizontal length) and the physical size. For the specified vapor flow rate, column diameters are calculated using the Aspen Tray Sizing module to be 0.95 and 0.80 m in the upper and lower sections, respectively. In the distillation column, weir height and tray pressure drop are set as 0.03 m and 0.01 bar per tray, respectively. The reflux drum has a diameter of 2 m and a length of 5 m with a total volume of 50 m^3 so that it could contain about 250 kmol of condensed liquid. Both pumps and valves are given

reasonable pressure drops to calculate pressure distribution. All parameters required by dynamic simulation are listed in Table 3.

Table 2: Simulation result of wastewater treatment process

Stream		FEED	WATER	$RECYCLE_W$	ESTER	DISTIL	SOLVENT
Content wt%	$H_2SO_4\times10^7$	0	22761.2	1.528	13824.5	12620.73	1×10^{-28}
	H_2O	0.96941	0.98572	0.33971	0.006472	0.05908	6.654×10^{-12}
	$C_4H_8O_2\times10^6$	958.86	8.0425	4194.98	4382.30	39656.62	43.112
	$C_4H_8O\times10^8$	642439	4.7816	52769852	2935351	26797504	0.1482
	$TMPD\times10^5$	316.425	19.542	95.798	150.809	1.7058	169.151
	$NaSO_4\times10^2$	0	1.1409	0	0.6930	6.3262	1×10^{-28}
	$TXIB\times10^6$	0	4.2289	83260.83	89210.75	53554.47	995260.31
	$NaC_4H_7O_2$	0.02004	0	0	0	0	0
Flowrate, kg/h		1042.9	1043.18	9.8124	228.231	25.00	200

Table 3: Parameters used in the dynamic simulation.

Unit	Diameter, m	Height, m	Pressure, atm	Temperature, K
EXTRACT	2	4	1	30
ESTERIZE	1	2	1	130
DISL	2	5	1	20
Valve	V1,V2	V3,V4,V5	V6,V7,V8,V9	V10,V11
Outlet pressure, atm	1	2	3	1
Valid phase	Liquid only	Liquid only	Liquid only	Liquid only
Pump	P1,P2	P3	P4,P5	P7
Pressure inc, atm	1	0.5	2	2.5

Figure 3 shows the initial flowsheet of dynamic simulation in Aspen Dynamics software. Some controllers are automatically installed, as listed in Table 4. These PID controllers include pressure controller PC, liquid level controller LC, flow controller FC, temperature controller TC and component controller NC.

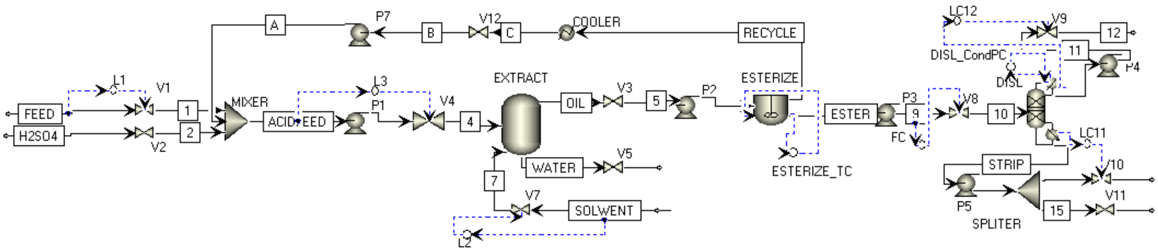

Figure 3: Initial dynamic simulation flowsheet

Table 4: Controller parameters.

Controller name	Gain Kc	Integration time Ti/min
Pressure controller	20	12
Liquid level controller	12	8
Flow controller	2	20
Temperature controller	10	9
Component controller	8	20

4.2 Discussion on the dynamic simulation result

Based on the aforementioned flowsheet and parameters, dynamic simulation is performed using Aspen Dynamics software. Its simulation results about water concentration within different streams are shown in Figure 4. WZmm(WATER), RZmm(WATER), EZmm(WATER), DZmm(WATER) denote the mass fraction of water at the bottom of Extract Column, in Recyclew, in Ester, and in DISL.

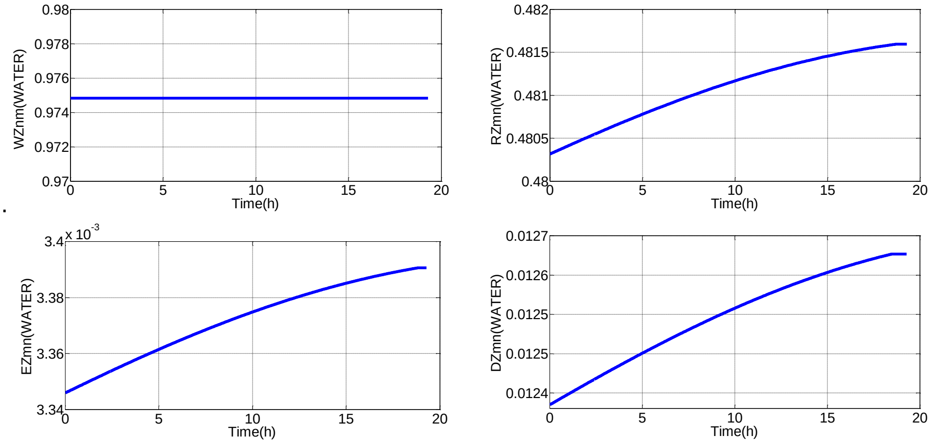

Figure 4: The dynamic trend of water mass fraction

It can be seen from Figure 4 that mass fraction of water at the bottom of extract column is stable even though the mass fraction of water in the recycle, ester feed, and distillate increase slightly with time elapsing. The mass fraction increases of water in these streams result from the switch disturb from steady-state simulation. The wastewater concentration after treatment reaches a stable level of 0.9748 at last. This simulation result approves the validity of the control structure shown in Figure 3. The stability of the system depicted in Figure 3 depends on the fluctuation control of process parameters within their expected range when facing outer disturbances. The step disturbances in extractant feed flowrate and reaction temperature are selected as two typical kinds of disturbance in this section to verify system stability. Figure 5 shows the mass fraction change of water in main streams when the mass flow rate of extractant feed stream is increased by 10 % after 3 h normal operation. WFmm(WATER), EFmm(WATER), DFmm(WATER) denote the flow rate of water at the bottom of Extract Column, in Ester, and in DISL. It can be seen that the control system given in Figure 3 is simple structurally and stable moderately in controlling the treatment quality of wastewater.

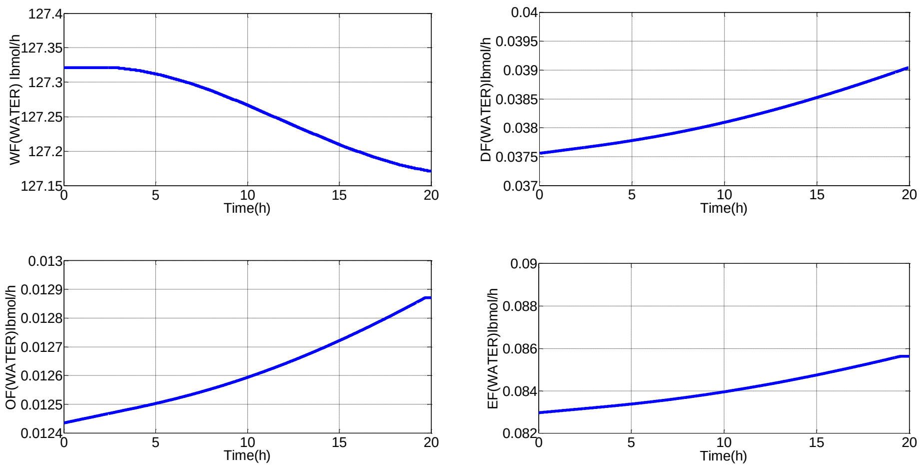

Figure 5: Effect of feed flowrate disturbances on system

4.3 Control scheme comparison

Three different control schemes are designed on the basis of the simple control system in order to find out the best control system at the specific scenario of disturbances. Based on the simple control system, control scheme I adds one cascade controller to regulate the bottom flow rate of extract column. Based on scheme I, control scheme II adds one temperature controller in the recycle stream to fully condense recycle components before entering extract column. Based on scheme I, control scheme III adds two flow rate controllers for sulfuric acid and recycle streams. Results show that the recovery time of four schemes are closely 55 h. All the control schemes can meet the treatment requirement of wastewater. In view of system complexity, control scheme I is simple and easy to control. But in view of system stability, scheme III has a short recovery time. Table 5 lists comparison of these four control schemes.

Table 5: Comparison of control schemes.

	Simple control system	Scheme I	Scheme II	Scheme III
Recovery time, h	60	58	56	52
Manipulated variable number	10	12	13	14

5. Conclusions

Aiming at the disposal of Eastman organic wastewater, this paper proposed one "waste control by waste" process. It uses an ester (trimethyl–pentanediol-di-isobutyl) produced by reacting trimethyl- pentanediol with isobutyric acid in the wastewater, as the extractant to avoid the recovery problem of the extractant. This wastewater treatment method was verified through simulation and experiment mixed method. COD is used to measure the treatment effect of organic wastewater. Simulation and experimental results show that the proposed wastewater treatment process can greatly reduce the organic content in wastewater and then prevent environmental pollution. Some basic data herein can be used as a reference to carry out further studies on optimization, industrial scale-up, safety analysis, etc. Future research will incorporate additional environmental considerations in the design process.

Acknowledgments

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