# Supplementary Information

## 1. Statistical analysis of RSM

The response variable was fitted using the response surface regression procedure by the following second order polynomial equation[9]:

$$Y = \beta_0 + \sum_{i=1}^{4}\beta_i X_i + \sum_{i=1}^{3}\sum_{j=i+1}^{4}\beta_{ij} X_i X_j + \sum_{i=1}^{4}\beta_{ii} X_i^2 \quad (1)$$

Where Y represents the predicted response of VFA/SCOD, $X_i$ and $X_j$ are the independent variables, and $\beta_0$ is a constant, $\beta_i$ is the *i*th linear coefficient, $\beta_{ij}$ is *ij*th interaction and $\beta_{ii}$ is the *i*th quadratic coefficient of the model. In this study the second-order polynomial equation can be described in Eq. (2):

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \\ & \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^3 + \beta_{44} X_4^4 \end{aligned} \quad (2)$$

Analysis of variance (ANOVA) was used for the regression analysis of the experimental data and the response surfaces. The quality fit of the polynomial model equation was expressed by the coefficient of determination ($R^2$), adjusted $R^2$ and adequate precision. The fitted polynomial equation was expressed as three-dimensional (3D) surface plots to visualize individual and interactive effect of factors on the response within the design range. Then, the optimum parameters involved in FW hydrolysis and acidification that resulted in the maximal conversion rate of SCOD to VFA were obtained by RSM.

## 2. ANOVA and model fitting

As shown in Table S3, the Model *F*-value of 217.61 with a very low probability value (*P*-value less than 0.0001) implied the model was significant. Values of "Prob > *F*" less than 0.05 indicated model terms were significant. In this case, *A*, *B*, *C*, *D*, *AB*, *AD*, *BC*, *CD*, $A^2$, $B^2$, $C^2$ and $D^2$ were significant model terms. The values greater than 0.10 indicated the model terms were not significant, and *AC* and *BD* were found to be insignificant. The "Lack of Fit *F*-value" of 9.04 further implied the Lack of Fit was significant and there was only a 1.27% chance that a "Lack of Fit *F*-value" this large could occur due to noise.

The fit of the model was also expressed by the coefficient of determination $R^2$, which was found to be 0.9951, indicating that the regression model was appropriate for simulating the experimental data. The "Pred *R*-squared" of 0.9829 was in reasonable agreement with the "Adj *R*-squared" of 0.9905, and both of them supported the significance of the model. At the same time, the relatively low value of variation coefficient 8.49% indicated a good precision and reliability of the model.

### *3. The variations of VFA production with fermentation time*

Fig. S2 shows the variations of total VFA productions in the 1#, 2# and 3# reactors during the anaerobic fermentation. The concentrations of total VFA were the sum of COD concentration converted from individual VFA using appropriate factors. It can be seen from Fig. S2 that the VFA productions were increased with fermentation time until that the steady states, and the growth rate of VFA in 3# was obviously quicker than other two reactors. The steady state in each reactor reached after about running 20 d. During the steady state, the VFA productions in 3# were much higher than those in 1# and 2#. The average VFA productions were 314.57, 168.38 and 867.42 mg COD per g-VS, respectively. Obviously, the optimum S/I of 5 can significantly improve the VFA production compared with sole FW and sole WAS fermentation. The higher VFA production in 3# was mainly attributed to the opportune operation conditions (T, SRT and OLR) and optimum substrate composition (S/I of 5), which was favorable for hydrolysis and acidogenesis of substrates, and inhibited for methanogenesis. Besides, the high-efficiency VFA production was also closely related to the pH variations in the reactors, which will be detailedly discussed in following section.

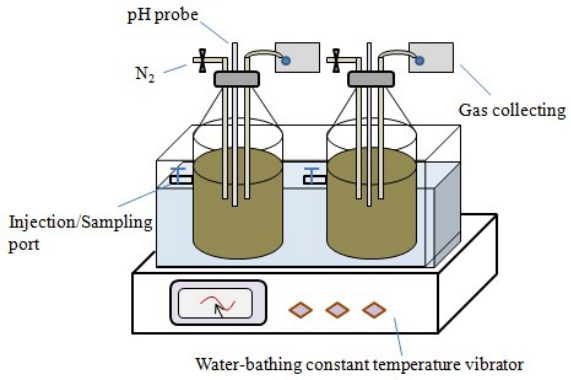


**Fig. S1** Semi-continuous anaerobic fermentation reactors.

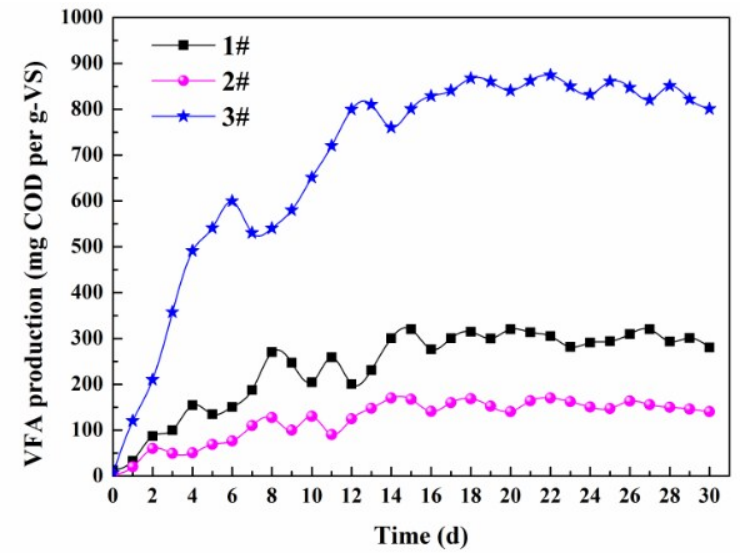


**Fig. S2** Variations of total VFA production with time in 1#, 2# and 3# reactors.

**Table S1** Levels and experimental range of variables for VFA production.

| Variable Name | Coded levels | | | | |
|---|---|---|---|---|---|
| | -2 | -1 | 0 | 1 | 2 |
| S/I | 3 | 4 | 5 | 6 | 7 |
| SRT (d) | 3 | 5 | 7 | 9 | 11 |
| OLR (g VS per L-d) | 4 | 6 | 8 | 10 | 12 |
| T ($^{o}$C) | 20 | 30 | 40 | 50 | 60 |

**Table S2** CCD experiments and the measured and predicted responses of VFA/SCOD.

| Run | Factors | | | | Response (%) | |
|---|---|---|---|---|---|---|
| | *A*: S/I | *B*: SRT (d) | *C*: OLR (g VS per L-d) | *D*: T ($^{o}$C) | Predicted | Actual |
| 1 | 5 | 7 | 8 | 20 | 20.46 | 20.95 |
| 2 | 4 | 9 | 10 | 30 | 49.17 | 49.48 |
| 3 | 4 | 9 | 6 | 30 | 50.12 | 48.66 |
| 4 | 4 | 5 | 10 | 30 | 45.23 | 45.19 |
| 5 | 6 | 9 | 6 | 30 | 48.01 | 48.86 |
| 6 | 6 | 9 | 10 | 30 | 51.32 | 52.48 |
| 7 | 6 | 5 | 6 | 30 | 45.12 | 45.29 |
| 8 | 4 | 5 | 6 | 30 | 40.24 | 40.21 |
| 9 | 6 | 5 | 10 | 30 | 53.23 | 53.08 |
| 10 | 5 | 7 | 8 | 40 | 88.95 | 88.40 |
| 11 | 5 | 7 | 8 | 40 | 87.97 | 88.40 |
| 12 | 5 | 3 | 8 | 40 | 57.82 | 57.37 |
| 13 | 5 | 11 | 8 | 40 | 70.34 | 68.99 |
| 14 | 5 | 7 | 8 | 40 | 89.32 | 88.40 |
| 15 | 5 | 7 | 8 | 40 | 87.33 | 88.40 |
| 16 | 5 | 7 | 8 | 40 | 88.56 | 88.40 |
| 17 | 5 | 7 | 8 | 40 | 88.27 | 88.40 |
| 18 | 5 | 7 | 4 | 40 | 58.13 | 58.10 |
| 19 | 5 | 7 | 12 | 40 | 72.34 | 70.57 |
| 20 | 3 | 7 | 8 | 40 | 40.12 | 40.85 |
| 21 | 7 | 7 | 8 | 40 | 60.38 | 57.85 |
| 22 | 4 | 9 | 10 | 50 | 53.1 | 55.02 |
| 23 | 6 | 5 | 10 | 50 | 60.21 | 63.77 |
| 24 | 6 | 9 | 10 | 50 | 67.20 | 66.93 |
| 25 | 6 | 9 | 6 | 50 | 57.32 | 59.45 |
| 26 | 4 | 5 | 10 | 50 | 48.13 | 46.98 |
| 27 | 6 | 5 | 6 | 50 | 52.73 | 52.13 |
| 28 | 4 | 9 | 6 | 50 | 50.48 | 50.34 |
| 29 | 4 | 5 | 6 | 50 | 37.20 | 38.13 |
| 30 | 5 | 7 | 8 | 60 | 35.62 | 33.33 |

**Table S3** ANOVA of CCD experimental results.

| Source | Sum of squares | df | Mean square | *F*-value | *P*-value (Prob > *F*) |
|---|---|---|---|---|---|
| Model | 9765.90 | 14 | 697.56 | 217.61 | < 0.0001 |
| *A* | 433.42 | 1 | 433.42 | 135.21 | < 0.0001 |
| *B* | 202.25 | 1 | 202.25 | 63.09 | < 0.0001 |
| *C* | 233.06 | 1 | 233.06 | 72.71 | < 0.0001 |
| *D* | 229.71 | 1 | 229.71 | 71.66 | < 0.0001 |
| *AB* | 23.79 | 1 | 23.79 | 7.42 | 0.0157 |
| *AC* | 7.83 | 1 | 7.83 | 2.44 | 0.1390 |
| *AD* | 79.34 | 1 | 79.34 | 24.75 | 0.0002 |
| *BC* | 17.33 | 1 | 17.33 | 5.41 | 0.0345 |
| *BD* | 14.12 | 1 | 14.12 | 4.40 | 0.0532 |
| *CD* | 14.92 | 1 | 14.92 | 4.65 | 0.0476 |
| $A^2$ | 2614.17 | 1 | 2614.17 | 815.52 | < 0.0001 |
| $B^2$ | 1090.40 | 1 | 1090.40 | 340.16 | < 0.0001 |
| $C^2$ | 992.82 | 1 | 992.82 | 309.72 | < 0.0001 |
| $D^2$ | 6433.44 | 1 | 6433.44 | 2006.97 | < 0.0001 |
| Residual | 48.08 | 15 | 3.21 | | |
| Lack of fit | 45.56 | 10 | 4.56 | 9.04 | 0.0127 |
| Pure error | 2.52 | 5 | 0.50 | | |
| Cor total | 9813.99 | 29 | | | |

**Table S4** The characteristics of hydrolyzed liquor of three reactors.

| Reactors | SCOD (g $L^{-1}$) | | | Carbohydrate (g $L^{-1}$) | | | Protein (g $L^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Initial | 20 d | IR (%) | Initial | 20 d | IR (%) | Initial | 20 d | IR (%) |
| 1# | 8.44 | 9.18 | 8.77 | 5.50 | 7.31 | 32.91 | 0.46 | 1.05 | 128.26 |
| 2# | 1.53 | 1.72 | 12.42 | 1.07 | 1.74 | 62.62 | 0.62 | 1.56 | 151.61 |
| 3# | 8.19 | 16.21 | 97.92 | 4.13 | 8.79 | 112.83 | 0.59 | 2.07 | 250.85 |

IR: Increasing rate

**Table S5** Peak locations and intensities from the EEM analysis of fermentation liquid.

| Reactors | Peak A (Ex/Em) | Int | Peak B (Ex/Em) | Int | Peak C (Ex/Em) | Int. |
|---|---|---|---|---|---|---|
| 1#-Initial | 225/340 | 251.5 | 280/345 | 359.9 | 255/472 | 506.4 |
| 1#-20 d | 225/344 | 411.8 | 280/343 | 636.6 | 255/475 | 569.9 |
| IR (%) | / | 63.7 | / | 76.8 | / | 12.5 |
| 2#-Initial | 240/355 | 123.8 | 280/345 | 175.7 | 250/447 | 410.7 |
| 2#-20 d | 225/356 | 264.9 | 280/347 | 419.2 | 250/439 | 459.6 |
| IR (%) | / | 113.9 | / | 138.6 | / | 11.9 |
| 3#-Initial | 225/340 | 203.7 | 280/347 | 277.8 | 250/461 | 361.2 |
| 3#-20d | 225/343 | 444.7 | 280/340 | 721.2 | 255/460 | 575.6 |
| IR (%) | / | 118.3 | / | 159.6 | / | 59.4 |

Int.: Intensity.

IR: Increasing rate.