ESI：Producing glyceric acid from glycerol via integrating vacuum dividing wall columns: conceptual process design and techno-economic-environmental analysis

Xin Zhou[1], Hao Yan[*1], Xiang Feng[*1], Hui Zhao[1], Yibin Liu[1], Xiaobo Chen[1], De Chen[1,2], Chaohe Yang[1]

1. State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao, Shandong 266580, People's Republic of China;

2. Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim 7491, Norway

[*]Corresponding Author: xiangfeng@upc.edu.cn; haoyan@upc.edu.cn.

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Summary of figures and tables

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1. Catalysts loading with TOF evaluation

Glycerol oxidation catalysts loading with TOF evaluation over PtRu/MCM-41 catalysts are listed in Table S1. As shown in Table S1, the Ru/MCM-41 catalyst is almost inactive for the glyceric acid oxidation. In contrast, the introduction of Pt greatly enhances the TOF from 328.1 to 823.9·h^{-1}. This clearly shows the promotional effect of Pt. The $Pt_{0.8}Ru_{0.8}$/MCM-41 catalyst exhibits excellent activity (TOF: 823.9·h^{-1}) and selectivity of glyceric acid in base-free medium, indicating that the structure formed between Pt and Ru promotes glycerol oxidation. More detailed description about catalysis such as the recyclability, characterization of the used catalysts can be found in our recently published work (Appl. Catal. B, 2019, 259, 118070).

Table S1. Oxidation of glycerol over PtRu/MCM-41 catalysts with different metal loading

Catalysts	Selectivity (%)[b]				Conversion(%)	TOF[c] (h^{-1})
	GLYAD	GLYA	DHA	GLYOA		
Pt/MCM-41[a]	8.7	60.1	12.1	8.8	47.3	328.1
$Pt_{0.8}Ru_{0.4}$/MCM-41[a]	16.1	64.4	10.3	2.0	56.7	670.9
$Pt_{0.8}Ru_{0.8}$/MCM-41[a]	4.8	74.1	8.2	4.6	69.2	823.9
$Pt_{0.8}Ru_{1.2}$/MCM-41[a]	10.1	69.4	11.1	3.2	54.9	694.6
$Pt_{0.8}Ru_{1.6}$/MCM-41[a]	21.7	58.8	12.6	0.4	47.4	337.6
Ru/MCM-41[a]	8.5	31.2	53.1	0.0	2.5	6.0
$Pt_{2.0}Ru_{2.0}$/MCM-41[d]	4.2	67.2	8.7	10.8	68.9	795.6
$Pt_{3.0}Ru_{3.0}$/MCM-41[d]	2.8	78.1	10.8	3.4	67.8	660.4
$Pt_{4.0}Ru_{4.0}$/MCM-41[d]	5.9	74.2	7.9	8.1	70.8	319.4

$Pt_{5.0}Ru_{5.0}$/MCM-41[d]	0.9	65.1	13.2	12.5	74.4	185.1

a. Reaction conditions: 0.2 catalyst, 25ml aqueous solution of glycerol (0.22 M), glycerol/Pt molar ratio 700, 80℃, 1MPa O_2, 8h

b. Most of the rest of the products are CO_2.

c. TOF was calculated as mole of glycerol molecules converted per mole of surface Pt atoms per hour. The conversion was all less than 10% to ensure that the average reaction rate is equal to the instantaneous reaction rate.

d. Reaction conditions: 0.2 catalyst, 25ml aqueous solution of glycerol (0.22 M), 80℃, 1MPa O_2, 4h

2. Process simulation and parameters

2.1. Boiling point and decomposition/condensation temperature

The specific temperature of decomposition or condensation of GA, GAD, DHA, GLY and GLA are shown in Fig. S1. As shown in Fig. S1, the normal boiling point of GA, GAD, DHA, GLY and GLA are 112℃, 227.5℃, 233.1℃, 287.9℃, and 324.3℃, respectively. The condensation or decomposition temperature of GA, GAD, DHA, GLY and GLA are 100℃, 149℃, 151℃, 204℃, and 239℃, respectively. Therefore, the separation of the above products could not be realized by conventional atmospheric distillation.

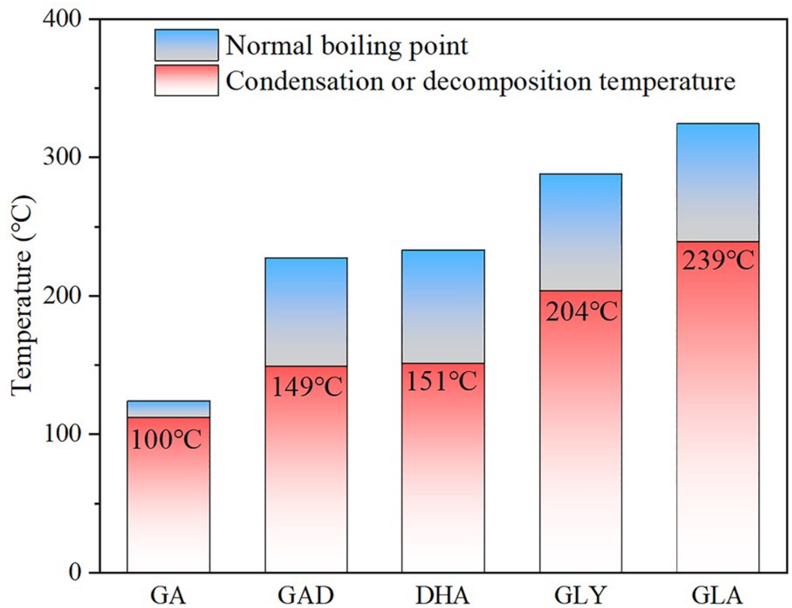

Fig. S1. The specific temperature of decomposition or condensation of GA, GAD, DHA, GLY and GLA.

In order to solve the energy utilization efficiency, the heat values of the glycerol selective oxidation products are listed in Table S2.

Table S2. The heat values of the glycerol selective oxidation products.

Items	Heat value/(MJ/kg)
GA	8.03
HPA	8.71
GAD	14.59
DHA	14.51
GLA	9.64
glycerol	17.96

2.2. Process simulation flowsheets

The simulation flowsheet of the conventional CGSO process under alkaline condition is shown in Fig. S2. In this process, GAD, HPA and GLA are the main products.

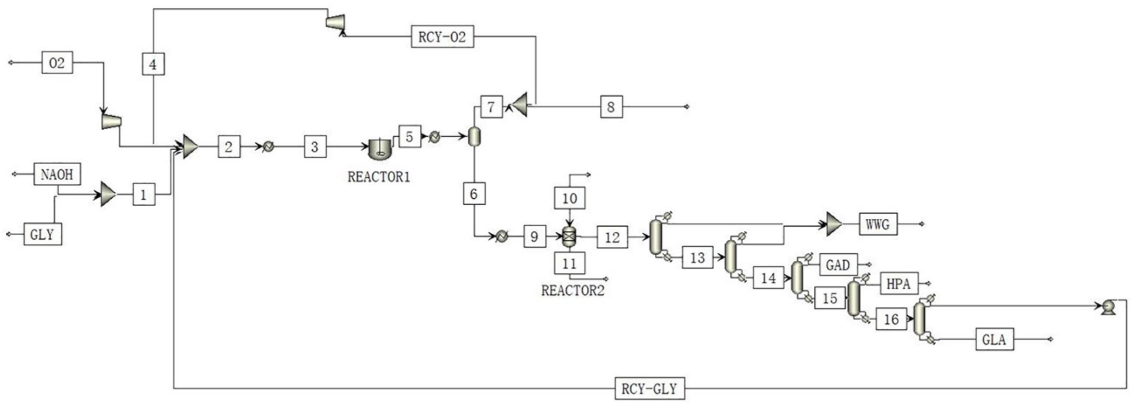

Fig. S2. The simulation flowsheet of the conventional CGSO process.

The simulation flowsheet of the VGSO process under base-free condition is described in Fig. S3. In this novel process, GAD, DHA and GLA are the main products. In addition, the feedstock glycerol can be recovered and recycled to react.

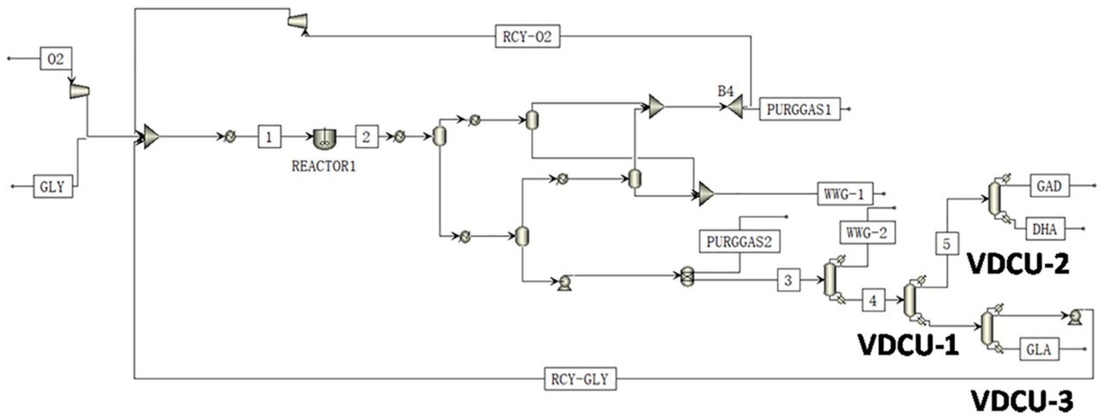

Fig. S3. The simulation flowsheet of the VGSO process.

The simulation flowsheet of the VDG process under base-free condition is described in Fig. S4. In this novel process, the vacuum dividing wall columns (VDWU-1 and VDWU-2) are integrated to enhance the separation of the glycerol oxidation products. The VDWU-1 and VDWU-2 are shown as the green box drew by dotted line. GAD, DHA and GLA are the main products. It should be noticed that the GA could be separated by the VDWU-2 under 100℃ successfully. Similarly, the feedstock glycerol can be recovered and recycled to react.

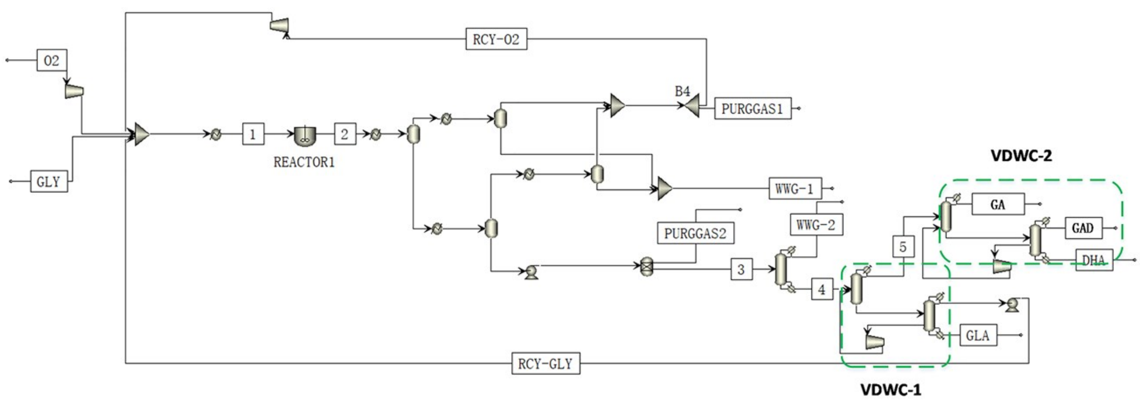

Fig. S4. The simulation flowsheet of the VDG process.

2.3. Detailed process simulation data

The detailed mass data and key unit parameters of the CGSO process are listed in Table S3. It should be noted that the material names are corresponding to the simulation flowsheet shown in Fig. S2.

Table S3. Detailed mass data and key unit parameters of the CGSO process.

	GLY	NaOH	3	5	7	9	12	WWG	14	GAD	HPA	GLA	RCY-GLY
Process Parameters													
Temperature/℃	25	25	60	60	30	25	40	100	102	133	154	230	200
Pressure/kPa	100	100	500	1000	600	100	100	100	7.2	6.7	6.9	6.1	6.3
Flowrates/(kg/h)	4607	5132	13303	13303	1670	9959	7106	481	5311	1420	207	1481	2203
Main Components (wt%)													
H_2O		0.67		0.07	0.005	0.95	0.06	0.99					
O_2			0.21	0.15	0.99								
H_2SO_4						0.05							
GLY	1		0.54	0.38	0.002		0.51		0.54	0.006	0.004	0.004	0.99
NaOH		0.33	0.25	0.25									0.004
FA				0.01	0.002		0.01	0.01					
GLA				0.14	0.001		0.18		0.20	0.004		0.98	
GAD				0.15			0.19		0.21	0.99	0.004	0.004	0.003
HPA				0.02			0.02		0.03		0.99		0.002
TA				0.01			0.01		0.02		0.001	0.01	0.01

The detailed mass data and key unit parameters of the VGSO process are shown in Table S4. It should be noted that the material names are corresponding to the simulation flowsheet shown in Fig. S3.

Table S4. Detailed mass data and key unit parameters of the VGSO process.

	O_2	GLY	1	2	WWG-1	WWG-2	4	5	GAD	DHA	GLA
Temperature/℃	25	25	80	80	30	88	93	98	123	137	229
Pressure/kPa	100	100	1000	1000	500	6	8	6	7	8	6
Flowrates/(kg/h)	545	1345	3570	3570	188	121	1893	200	123	77	1233
<u>Components</u>											
H_2O			0.01	0.08	0.89	0.92					
O_2	1		0.47	0.34	0.04						
GLY		1	0.51	0.13	0.001		0.25				0.008
FA			0.006	0.01	0.04	0.03					
GA			0.002	0.02	0.02		0.03	0.19	0.008	0.003	
GLA				0.36	0.003		0.63				0.992
GAD			0.001	0.04	0.003		0.05	0.52	0.992	0.002	
DHA			0.001	0.02	0.003		0.03	0.29		0.995	

The detailed mass data and key unit parameters of the VDG process are shown in Table S5. It should be noted that the material names are corresponding to the simulation flowsheet shown in Fig. S4.

Table S5. Detailed mass data and key unit parameters of the VDG process.

	O_2	GLY	1	2	WWG-1	WWG-2	4	5	GA	GAD	DHA	GLA
Temperature/℃	25	25	80	80	30	85	95	97	88	121	139	227
Pressure/kPa	100	100	1000	1000	500	6	8	6	6	7	8	6
Flowrates/(kg/h)	545	1342	3545	3545	187	106	1933	237	42	121	74	1238
<u>Components</u>												
H_2O			0.01	0.08	0.90	0.93						
O_2	1		0.47	0.35	0.04							
GLY		1	0.51	0.13	0.001		0.24		0.992			0.005
FA			0.006	0.01	0.03	0.07						
GA			0.002	0.02	0.02		0.02	0.18		0.006	0.002	
GLA				0.35	0.004		0.64					0.995
GAD			0.001	0.04	0.003		0.06	0.51	0.05	0.994	0.001	
DHA			0.001	0.02	0.002		0.04	0.31	0.03		0.997	

2.4. Reaction network and kinetic parameters

The reaction routines of VGSO and VDG process under base-free condition is shown in Fig. S5. As shown in this figure, seven selective oxidation reactions numbered R1-R7 are involved in the VGSO and VDG process. The main products of glycerol selective oxidation, including GAD, DHA and GLA are shown as the red box drew by dotted line.

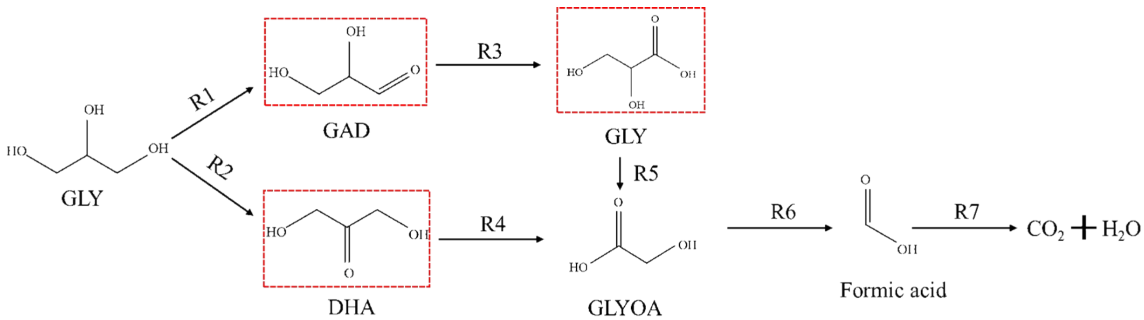

Fig. S5. The reaction routines of the VGSO and VDG processes.

The kinetic parameters are listed in Table S6. It should be mentioned that the reaction numbers are corresponding to the reaction routines shown in Fig. S5.

Table S6. The kinetic parameters for the VGSO and VDG processes.

No.	Reactions	k_0	E/(J/kmol)
R1	$0.5O_2+C_3H_8O_3 \rightarrow C_3H_6O_3+H_2O$	7.96e+06	4.13e+07
R2	$0.5O_2+C_3H_8O_3 \rightarrow C_3H_6O_3+H_2O$	7.65e+07	5.50e+07
R3	$0.5O_2+C_3H_6O_3 \rightarrow C_3H_6O_4$	1.20e+04	2.34e+08
R4	$1.5O_2+C_3H_6O_3 \rightarrow C_2H_4O_3+H_2O+CO_2$	2.25e+08	6.90e+07
R5	$0.5O_2+C_3H_6O_4 \rightarrow C_2H_4O_3+CH_2O_2$	8.82e+15	1.08e+08
R6	$O_2+C_2H_4O_3 \rightarrow CH_2O_2+CO_2+H_2O$	4.98e+05	5.81e+07
R7	$0.5O_2+CH_2O_2 \rightarrow CO_2+H_2O$	4.85e+05	5.84e+07

3. Techno-economic analysis and estimation parameters

3.1. Parameters for techno-economic analysis

The list of equipment and installed costs for calculating total capital investment by Aspen Process Economic Analyzer of the CGSO, VGSO and VDG processes are shown in Tables S7, S8 and S9, respectively. It should be mentioned that the summary of equipment and installed costs for waste water treatment process are shown in Table S10. For comprehensive analysis of Table S7-S9, the total capital investment for the CGSO process is 1.39×10^8 USD dollars, and the largest portion of the cost was the installation costs (8.50×10^7 USD dollars, 61.2% of the capital investment). As for the VGSO process, the total capital investment is 1.28×10^8 USD dollars, and the largest portion of the cost is also the installation costs (6.46×10^7 USD dollars, 50.5% of the capital investment). The total capital investment of the VDG process is the least, 1.23×10^8 USD dollars, and similarly, the largest portion of the cost is also the installation costs (6.71×10^7 USD dollars, 54.6% of the capital investment).

Table S7. The list of equipment and installed costs for calculating total capital investment of the CGSO process.

Equipment name	Number required	Configuration	Equipment costs	Installed costs
Pumps	1	Centrifugal pump	4.41×10^5	8.37×10^5
Heat exchanges	3		9.77×10^5	2.65×10^6
Flash tank	1	Single stage flash tank	5.22×10^5	8.39×10^5
Compressor	2		2.82×10^6	4.76×10^6
Reactors	2	Batch reactor	6.33×10^6	1.03×10^7
Distillation columns	2	20-stage; 25-stage	9.20×10^6	1.87×10^7

Vacuum distillation columns	3	22-stage; 27-sateg; 55-stage	1.81×10^7	3.49×10^7
Total			3.84×10^7	7.50×10^7

Table S8. The list of equipment and installed costs for calculating total capital investment of the VGSO process.

Equipment name	Number required	Configuration	Equipment costs	Installed costs
Pumps	2	Centrifugal pump	6.37×10^5	1.16×10^6
Heat exchanges	5		2.38×10^6	4.89×10^6
Flash tank	4	Single stage flash tank	2.62×10^6	1.74×10^6
Compressor	2		2.21×10^6	4.31×10^6
Reactors	1	Batch reactor	3.59×10^6	6.36×10^6
Distillation columns	1	15-stage	3.40×10^7	1.26×10^7
Vacuum distillation columns	3	20-stage; 28-sateg; 50-stage	1.62×10^7	3.35×10^7
Total			6.16×10^7	6.46×10^7

Table S9. The list of equipment and installed costs for calculating total capital investment of the VDG process.

Equipment name	Number required	Configuration	Equipment costs	Installed costs
Pumps	2	Centrifugal pump	6.37×10^{5}	1.16×10^{6}
Heat exchanges	5		2.38×10^{6}	4.89×10^{6}
Flash tank	4	Single stage flash tank	2.62×10^{6}	1.74×10^{6}
Compressor	2		2.21×10^{6}	4.31×10^{6}
Reactors	1	Batch reactor	3.59×10^{6}	6.36×10^{6}
Vacuum distillation columns	1	10-stage	2.54×10^{7}	1.12×10^{7}
VDWU	2	20-stage; 28-sateg; 50-stage	1.57×10^{7}	3.74×10^{7}
Total			5.25×10^{7}	6.71×10^{7}

Table S10. Summary worksheet for the estimated parameters, project cost including total capital investment and waste water treatment [1-3].

Items	Units	CGSO	VGSO	VDG
Equipment costs	USD dollars	4.43×10^{7}	6.16×10^{7}	5.25×10^{7}
Installed costs	USD dollars	8.50×10^{7}	6.46×10^{7}	6.71×10^{7}
Waste water treatment system	USD dollars	2.6×10^{7}	3.52×10^{6}	3.31×10^{6}
Catalysts	USD dollars	1.91×10^{7}	1.83×10^{7}	1.77×10^{7}
Total capital investment	USD dollars	1.74×10^{8}	1.38×10^{8}	1.33×10^{8}
Interest rate	-		8%	
Operating time	hours/year		8400	
Production load	-		100%	
Project construction period	year		2	
Salaries	USD dollars /person/year		10000 $	
Number of workers	person		50	
Net salvage rate	%		5%	
Discounted annual rate	%		15%	
Benchmark IRR	%		⩾12%	
Life cycle of plant	year		20	
Tax rate	%		25%	

The feedstock, products and utilities of total production costs estimated in this study are listed in Table S11 [4-6].

Table S11. The prices of feedstock, products and utilities of total production costs for the CGSO, VGSO and VDG processes.

Items	Unit	Value
Glycerol	USD dollars/t	510
Glyceric acid	USD dollars/t	3625
O_2	USD dollars/t	142.77
glycolic acid	USD dollars/t	1810
glyceraldehyde	USD dollars/t	1850
dihydroxyacetone	USD dollars/t	1850
hydroxypyruvic acid	USD dollars/t	1825
Fresh water	USD dollars/MJ	0.009
Recycle cooling water	USD dollars/MJ	0.006
Low pressure Steam	USD dollars/MJ	0.039
Medium pressure Steam	USD dollars/MJ	0.042
Electricity	USD dollars/(kW·h)	0.07
Fuel oil/Fuel gas	USD dollars/MJ	0.014

3.2. NPV results with the scale-up experimental data

Different experimental results in scale-up would clearly impact the techno-economic analysis. Hence, a series scale-up experiments were carried out based on the PtRu/MCM-41 catalysts, and shown in Fig S6. From Fig. S6 it can be seen that VDG and VGSO processes have good economic benefits even when the reactor is enlarged to 10L.

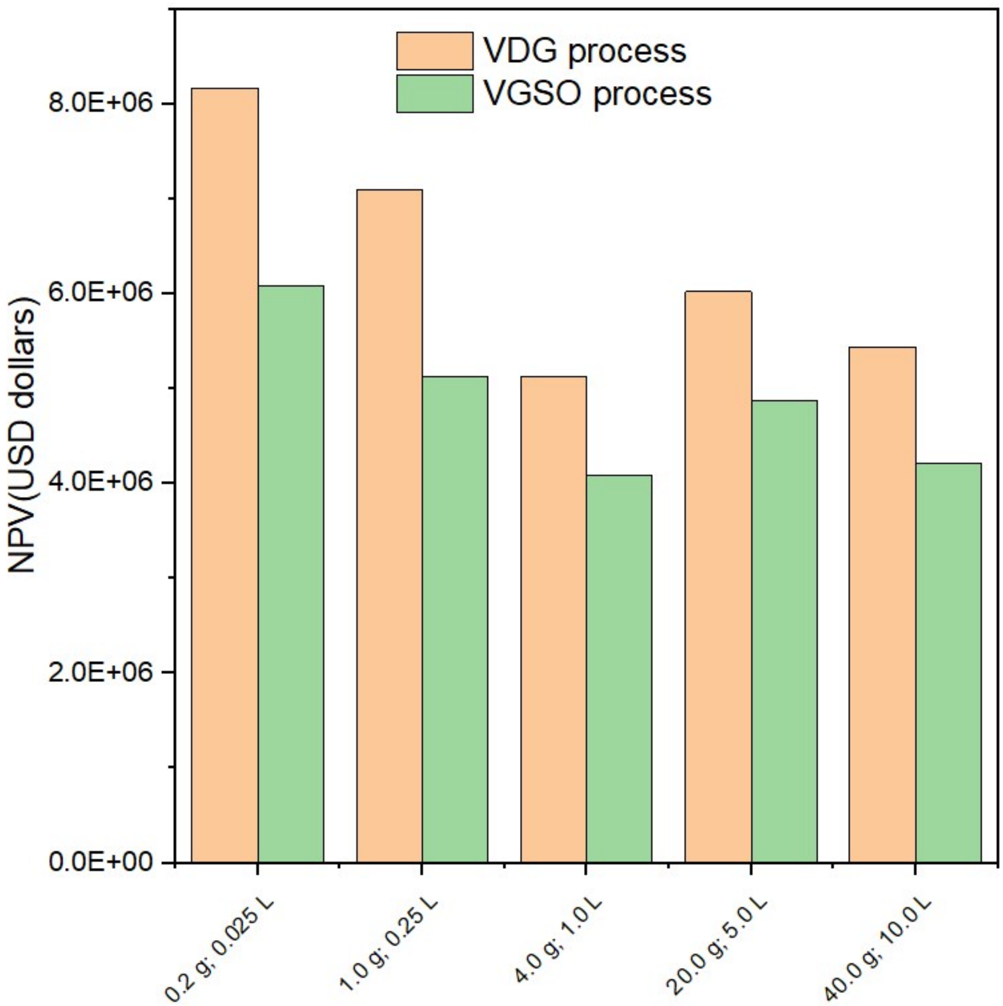

Fig. S6. NPV results with the scale-up experimental data.

3.3. Sensitivity analysis

The sensitivity analysis of the CGSO and VGSO process are performed in Fig. S7 and Fig. S8, respectively.

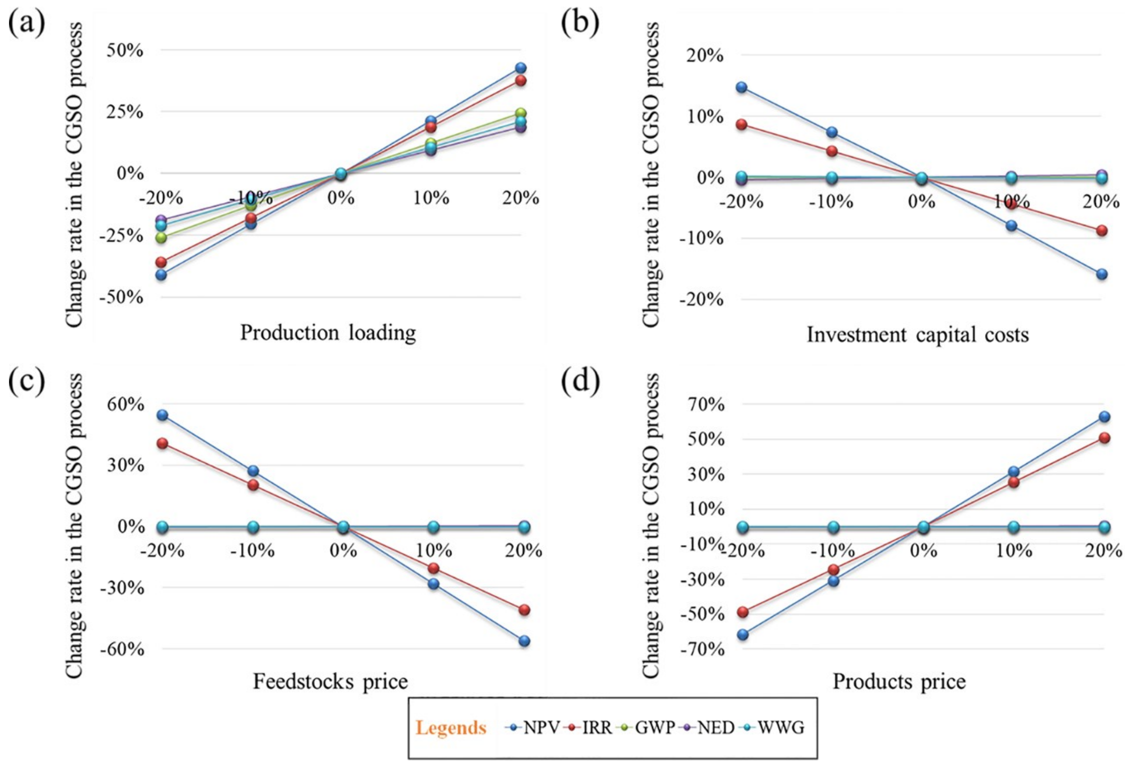

Fig. S7. Results of sensitivity analysis for the four parameters in the CGSO process: (a) production loading; (b) investment capital costs; (c) feedstocks price; and (d) products price.

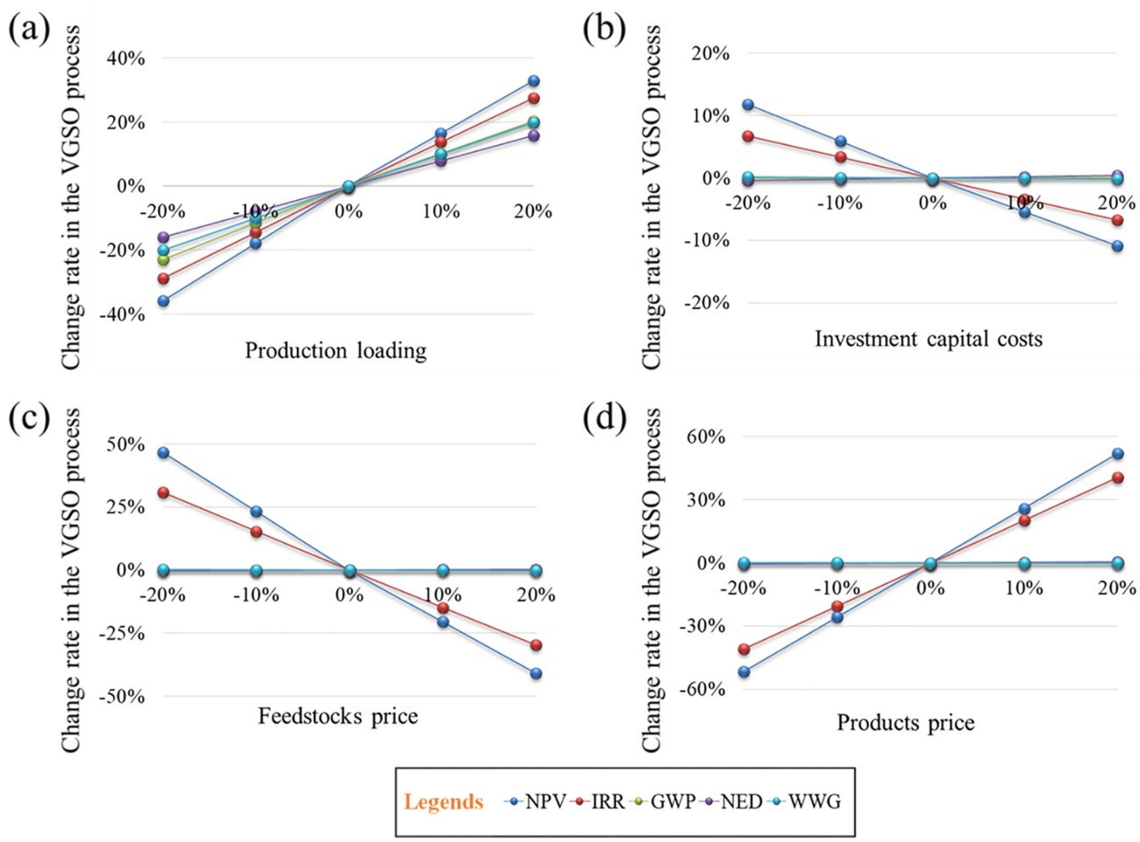

Fig. S8. Results of sensitivity analysis for the four parameters in the VGSO process: (a) production loading; (b) investment capital costs; (c) feedstocks price; and (d) products price.

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