

A Sulfuric Acid Management Strategy for the Production of Liquid Hydrocarbon Fuels via Catalytic Conversion of Biomass-derived Levulinic Acid

Supplementary information

S.1. Power cycle

In a power cycle, heat input is converted into the mechanical output, and finally to electricity, while heat pump cycles transfer heat from low to high temperatures using mechanical work input. Most plants operate based on modifications of a Rankine cycle, which is depicted in Figure S.1. Superheated steam at high pressure is supplied into a turbine to produce a drier steam after expansion since water droplet formation reduces the steam turbine efficiency as water droplets hit the turbine blades.¹ Turbine rejects low-pressure steam or wet steam at the outlet. Before pressurizing the turbine outlet, low-pressure steam or wet steam should be condensed to water to reduce the amount of work required. In a real process, inlet to a pump should be subcooled to avoid cavitation, which occurs when vapor bubbles prevent the pump from drawing the liquid into the pump cavity.² After pressurizing water using a pump, superheated steam is regenerated before entering the turbine in a boiler/superheater by integrating the heat of hot combustion gases produced in a fired heater. In actual power plants, separate boiler and superheater are typically used, which is not shown in Figure S.1(a) for the sake of simplicity. In practice, the compression by the pump and the expansion in the turbine are non-reversible and entropy increases during these processes.³ Therefore, power required by the pump increases, while power generated by the turbine decreases.

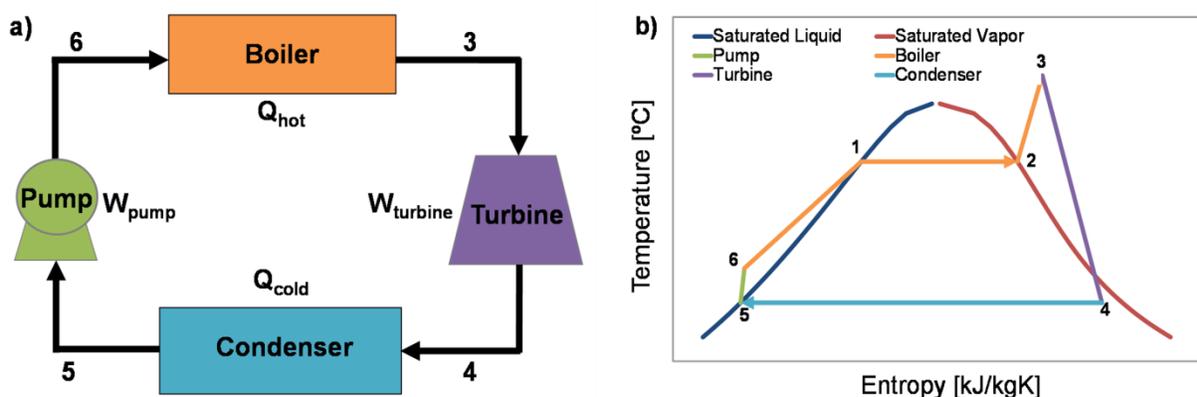


Figure S.1. The Rankine Cycle. a) Representation of the Rankine cycle and b) temperature-entropy diagram for the Rankine cycle (adapted from Elliott and Lira²).

S.2. Heat recovery network

Transformation of raw materials into final products in a chemical plant also involves heating and cooling operations of process streams. Exclusive use of industrial utility streams (such as steam, hot oil, cooling water, etc.) in these heating and cooling operations results in high operating costs. As an alternative, heat recovery networks allow the exchange of heat among the process streams in order to reduce the total utility consumption. In this way, part of the heat in the process streams that need cooling, can be transferred to other process streams that need heating. However, in general, due to the restrictions imposed by the second law of thermodynamics, this heat exchange among process streams does not cover all the cooling-

heating requirements. This is why in almost every chemical plant the use of industrial utilities is needed.⁴ In Figure S.2, we present a heating-cooling diagram (temperature vs. heat) and a heat exchanger and heater/cooler network for a process with only one hot stream and one cold stream.

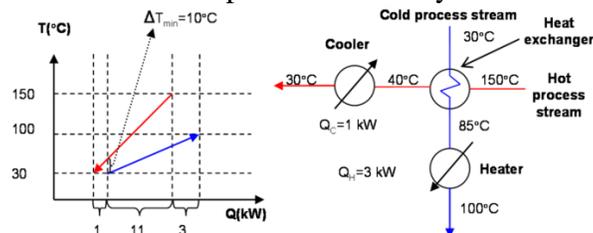


Figure S.2. A simple heating-cooling network.

For this simple case, the overlapping of the curves in the T vs. Q diagram represents the recovered heat (11 kW), and the other segments represent the cooling ($Q_C=1$ kW) and heating ($Q_H=3$ kW) requirements. In order to estimate the minimum requirement for industrial utilities in a generic chemical plant, the maximum heat recovery should be obtained in a heat exchange operation. This operation is referred in the literature as a *heat cascade*. In this cascade, the initial and final temperatures (T_s , T_t) of all process streams and available utility streams are shifted by fixing the minimum approach temperature (ΔT_{\min}) between hot and cold streams ($-\Delta T_{\min}/2$ for the hot streams i.e. those with $T_s > T_t$; and $+\Delta T_{\min}/2$ for the cold streams i.e. those with $T_s < T_t$). Later, these temperatures are sorted in a list that defines temperature intervals $k=1, \dots, K$. At this point, the problem can be modeled as a linear programming (LP) trans-shipment problem.⁵ Hot utilities and process streams (origin nodes) supply heat to the temperature intervals (intermediate nodes), and these intervals supply heat to adjacent lower temperature intervals, cold utility streams and process streams. The established heat flow pattern guarantees maximum heat transfer, while satisfying the second law of thermodynamics (heat can only be transferred from high temperature sources to low temperature sinks) and the ΔT_{\min} for the design of the heat exchangers in the network. Figure S.3 represents the temperature intervals and the trans-shipment diagram for the example presented in Figure S.2 including two utility streams.

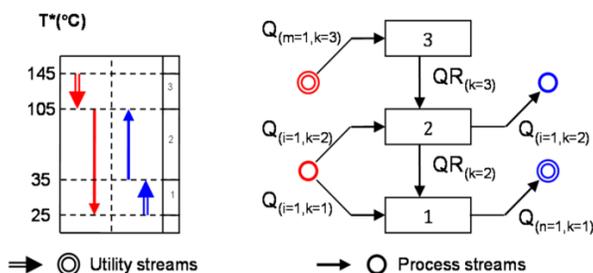


Figure S.3. (a) Shifted temperature scale (T^*) and temperature intervals. (b) Heat cascade as a trans-shipment model.

For this problem, we define the sets and basic stream information as follows:

$$\text{Hot streams} = \{i \mid i = 1, \dots, NH\} [F_i, (C_p)_i, T_i^s, T_i^t]$$

$$\text{Cold streams} = \{j \mid j = 1, \dots, NC\} [F_j, (C_p)_j, T_j^s, T_j^t]$$

$$\text{Hot utilities} = \{m \mid m = 1, \dots, NS\} [(F_{\max})_m, (C_p)_m, T_m^s, T_m^t, UP_m]$$

$$\text{Cold utilities} = \{n \mid n = 1, \dots, NW\} [(F_{\max})_n, (C_p)_n, T_n^s, T_n^t, UP_n]$$

where F [kg/s] is the flow rate, F_{max} [kg/s] is the utility availability, C_p [kJ/kg.K] is the heat capacity, and UP is the utility unit price. Heat capacity and unit price of utilities are given in Table S.1. Using this values, the heat associated to every process (i,j) in every temperature interval (k) it crosses can be calculated by:

$$Q_{ik} = F_i \times (C_p)_{ik} \times \Delta T_k \quad (\text{Heat supplied by hot process stream } i \text{ to interval } k)$$

$$Q_{jk} = F_j \times (C_p)_{jk} \times \Delta T_k \quad (\text{Heat taken by cold process stream } j \text{ from interval } k)$$

The initial unknown heat associated to every utility stream (m,n) in every temperature interval (k) are related to the stream characteristics by:

$$Q_{mk} = F_m \times (C_p)_{mk} \times \Delta T_k \quad (\text{Heat supplied by hot utility stream } m \text{ to interval } k)$$

$$Q_{nk} = F_n \times (C_p)_{nk} \times \Delta T_k \quad (\text{Heat taken by cold utility stream } n \text{ from interval } k)$$

In this way, considering the heat balance in every temperature interval, the problem of finding the minimum cost set of required utilities is given by:

$$\begin{aligned} \min \quad & \text{UtilityCost} = \sum_m UP_m \times F_m + \sum_n UP_n \times F_n \\ \text{s.t.} \quad & QR_{k+1} + \sum_i Q_{ik} + \sum_m F_m \times (C_p)_{mk} \times \Delta T_k = QR_k + \sum_j Q_{jk} + \sum_n F_n \times (C_p)_{nk} \times \Delta T_k, \quad k = 1, \dots, K \\ & F_m \leq (F_{max})_m, \quad F_n \leq (F_{max})_n, \quad F_m, F_n \geq 0 \\ & QR_1 = QR_{K+1} = 0 \\ & QR_k \geq 0, \quad k = 1, \dots, K \end{aligned}$$

Table S.1. Unit utility properties (modified from Turton *et al.*⁶).

Utility		Properties		
		Cp [kJ/kg.°C]	Cost [\$/GJ]	Cost [\$/ton]
Boiler Steam	Low Pressure (5 barg, T _{Supply} =160°C - T _{Return} =159°C)	2105	14.05	29.58
	Mid Pressure (10 barg, T _{Supply} =184°C - T _{Return} =183°C)	2022	14.83	29.99
	High Pressure (41 barg, T _{Supply} =254°C - T _{Return} =253°C)	1748	17.70	30.94
Cooling Water	(T _{Supply} =30°C, T _{Return} =40°C)	4.32	0.345	0.0148
Thermal Fluids	High Temperature (T _{Supply} =400°C - T _{Return} =399°C)	206	12.33	2.53

References

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2. J. R. Elliott and C. T. Lira, in *Introductory Chemical Engineering Thermodynamics*, Prentice Hall, New Jersey, 1st edn., 1999.
3. F. Xu, D. Y. Goswami and S. S. Bhagwat, *Energy*, 2000, **25**, 233-246.
4. L. T. Biegler, I.E. Grossmann and A. W. Westerberg, in *Systematic Methods of Chemical Process Design*, Prentice Hall, New Jersey, 1st edn., 1997.
5. S. A. Papoulias and I. E. Grossmann, *Computers & Chemical Engineering*, 1983, **7**, 707-721.
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S.3. Process flow diagram

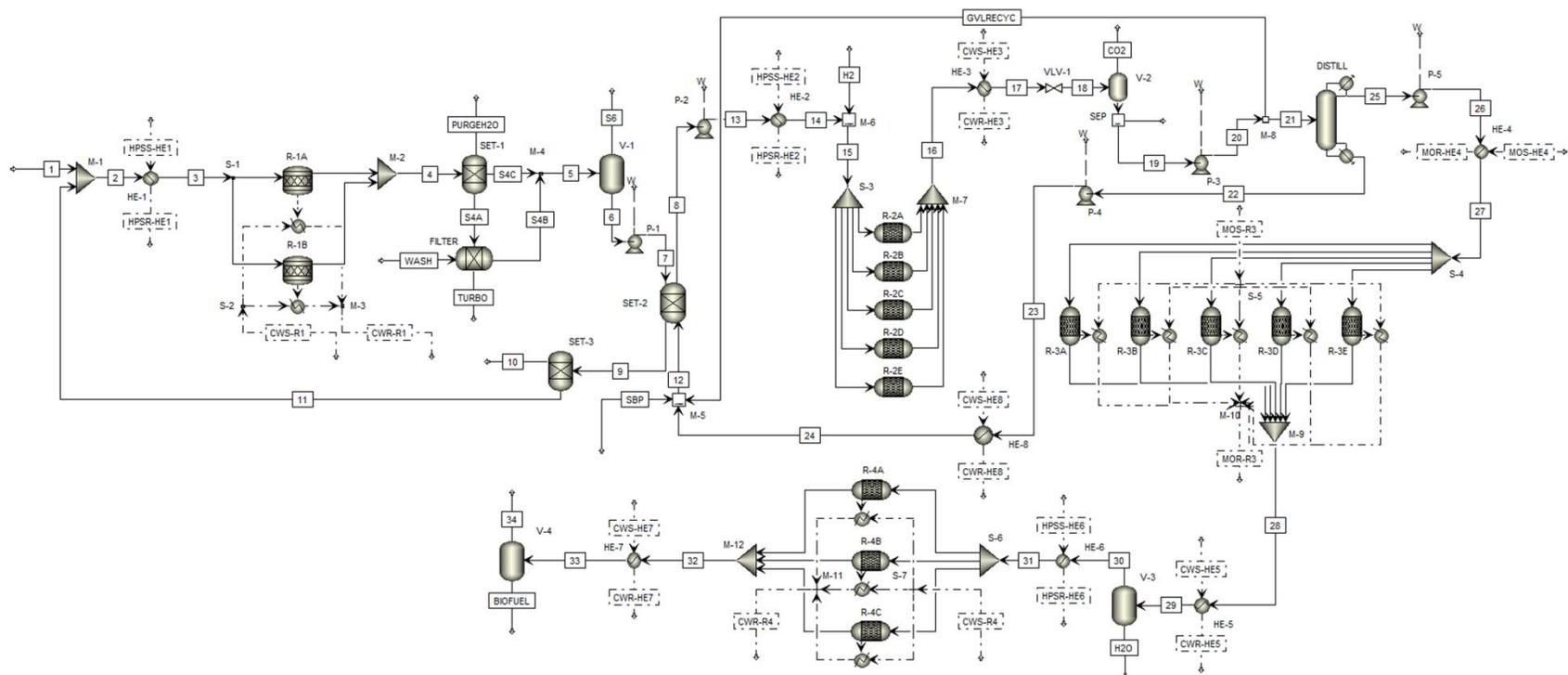


Figure S.4. Detailed process flow diagram of the improved alkylphenol strategy.

Table S.2. Information of important process streams.

Mass Flow (kg/hr)	1	3	4	7	8	9	12	15	16	21	22	27	28	31	33	BIOFUEL
Sulfuric Acid	2386.2	2386.2	2386.2	2339.9	0.0	2339.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Water	48697.9	48697.9	50412.0	7299.2	0.0	7299.2	0.0	0.0	1671.8	1547.6	0.0	1547.6	1547.6	90.2	90.2	89.9
C ₆ sugars	31166.7	31166.7	14025.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Lignin	16777.7	16777.7	16777.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
FA	0.0	338.0	4717.3	476.1	138.1	338.0	0.0	138.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
LA	0.0	0.0	11048.3	10668.6	10668.6	0.0	0.0	10668.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
GVL	0.0	5.8	5.7	4.3	186.2	5.8	187.6	186.2	9290.4	9264.9	187.6	9077.3	90.8	0.5	0.5	0.5
CO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	132.0	5.1	0.0	5.1	3955.4	3942.6	3942.6	29.0
H ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	193.5	10.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₄ H ₈	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5036.2	5036.0	50.4	0.1
C ₈ H ₁₆	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1495.7	1485.1
C ₁₂ H ₂₄	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1296.3	1296.1
C ₁₆ H ₃₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1246.4	1246.4
C ₂₀ H ₄₀	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	947.3	947.3
SBP	0.0	0.0	0.0	0.0	91179.0	0.0	91179.0	91179.0	88256.3	88212.7	88024.3	188.3	188.3	0.2	0.2	0.2
MTHF	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	79.1	72.2	0.0	72.2	72.2	10.3	10.3	10.2
Total Mass Flow (kg/hr)	99028.5	99372.3	99372.2	20788.0	102171.8	9982.9	91366.6	102365.3	99440.3	99102.4	88212.0	10890.4	10890.4	9079.9	9079.9	5104.8
Temperature (K)	463.1	473.0	473.1	376.4	453.0	453.0	473.0	492.6	493.0	379.7	512.3	648.1	648.1	443.0	313.1	294.8
Pressure (atm)	15.8	15.4	15.2	16.2	15.5	15.5	15.7	35.5	35.4	1.0	1.0	36.4	35.9	35.5	34.8	34.7
Enthalpy Flow (Gcal/hr)	-235.2	-235.0	-237.8	-47.2	-45.4	-31.6	-29.8	-42.7	-44.5	-49.2	-26.6	-12.6	-12.1	-8.4	-10.4	-2.1

S.4. Alternative process configurations

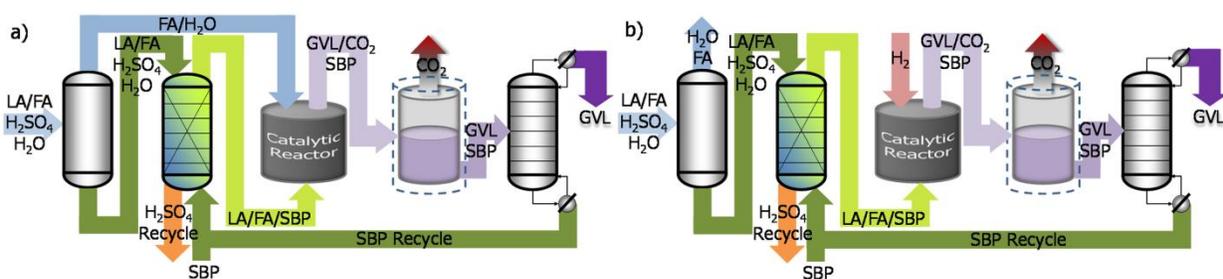


Figure S5. Alternative process configurations for the alkylphenol-based separation. a) Formic acid as the hydrogen source and b) external hydrogen supply. LA, levulinic acid; FA, formic acid; GVL, γ -valerolactone; SBP, 2-sec-butyl phenol.