

Phenol Wastewater Treatment with Supercritical CO₂

Background

Wastewater containing phenol is generated in many of the steel industry's coking facilities. A typical concentration for phenol in the effluent water is 6.8 wt%. Before this water can be released to the environment, the phenol concentration must be reduced to 39 ppb.

One method for removal of phenol from wastewater is extraction using supercritical CO₂. We have found this method to be economically competitive with the alternatives. These alternatives include incineration, wet air oxidation (supercritical water oxidation), and biological processes.

Environmental Significance

Waste stream treatment

Use of an environmentally-benign solvent

Process Description

The PFD is attached. The wastewater in Stream 1 is pumped and cooled to the extractor operating conditions. The extractor, T-301, is run countercurrently. Essentially all the phenol is removed from the water. In Stream 3, the treated water contains some residual CO₂ and is throttled and heated to degas the water. The CO₂ is then recycled in Stream 6. The treated water is then cooled and throttled to atmospheric pressure.

The supercritical CO₂, some water, and all of the phenol exit the top of the extractor and are throttled and heated to allow the CO₂ to become a gas and separate from the water and phenol in V-302. The CO₂ is recycled in Stream 4 while the water and phenol proceed to T-302 for separation. In T-302, the water and any residual CO₂ are taken off of the top of the column. In V-303, the residual CO₂ is recycled in Stream 10. Part of the water is used as reflux for the

column, and the rest is recycled to the wastewater feed stream. The phenol leaving the bottom of the column is essentially pure and is subcooled and throttled to atmospheric pressure for storage.

The residual CO₂ in Stream 10 is compressed and is combined with the CO₂ in Streams 4 and 6. The CO₂ is then compressed and cooled to the operating conditions for recycle into the extractor. Essentially all of the CO₂ is recovered and recycled. However, if any make-up CO₂ is needed, it can be added to the CO₂ stream entering the extractor.

Necessary Information and Simulation Hints

In the tower, a partial condenser is used; however, it is desired to remove CO₂ gas and only reflux part of the liquid water. In order to do this, a tower without a condenser was used and the condenser, separation vessel, and water split were added as separate units.

For non-supercritical conditions, ideal vapor pressure with LLV three-phase K-values was used. There may be better alternatives to this choice. Peng-Robinson was used as the enthalpy model. For the extraction unit, no thermodynamic model would predict literature values. Therefore, T-301 was modeled as a component separator with outlet conditions based on published data¹.

Equipment Descriptions

P-301 A/B	Wastewater pump
T-301	Extraction tower
E-301	Wastewater cooler
E-307	CO ₂ recycle cooler
E-302	Raffinate heater
E-303	Extract heater
C-303	Recycle compressor

V-301	Degasser
V-302	Degasser
E-304	Reboiler for T-302
E-305	Condenser for T-302
T-302	Phenol tower
P-303 A/B	Reflux pump
V-303	Reflux drum
C-301	Recycle compressor
E-306	Recycle intercooler
C-302	Recycle compressor
E-308	Phenol cooler
E-309	Water cooler

References

1. Ghonsagi, D., S. Gupta, K. M. Dooley, and F. C. Knopf, *The Journal of Supercritical Fluids*, **4**, 53-59 (1991).

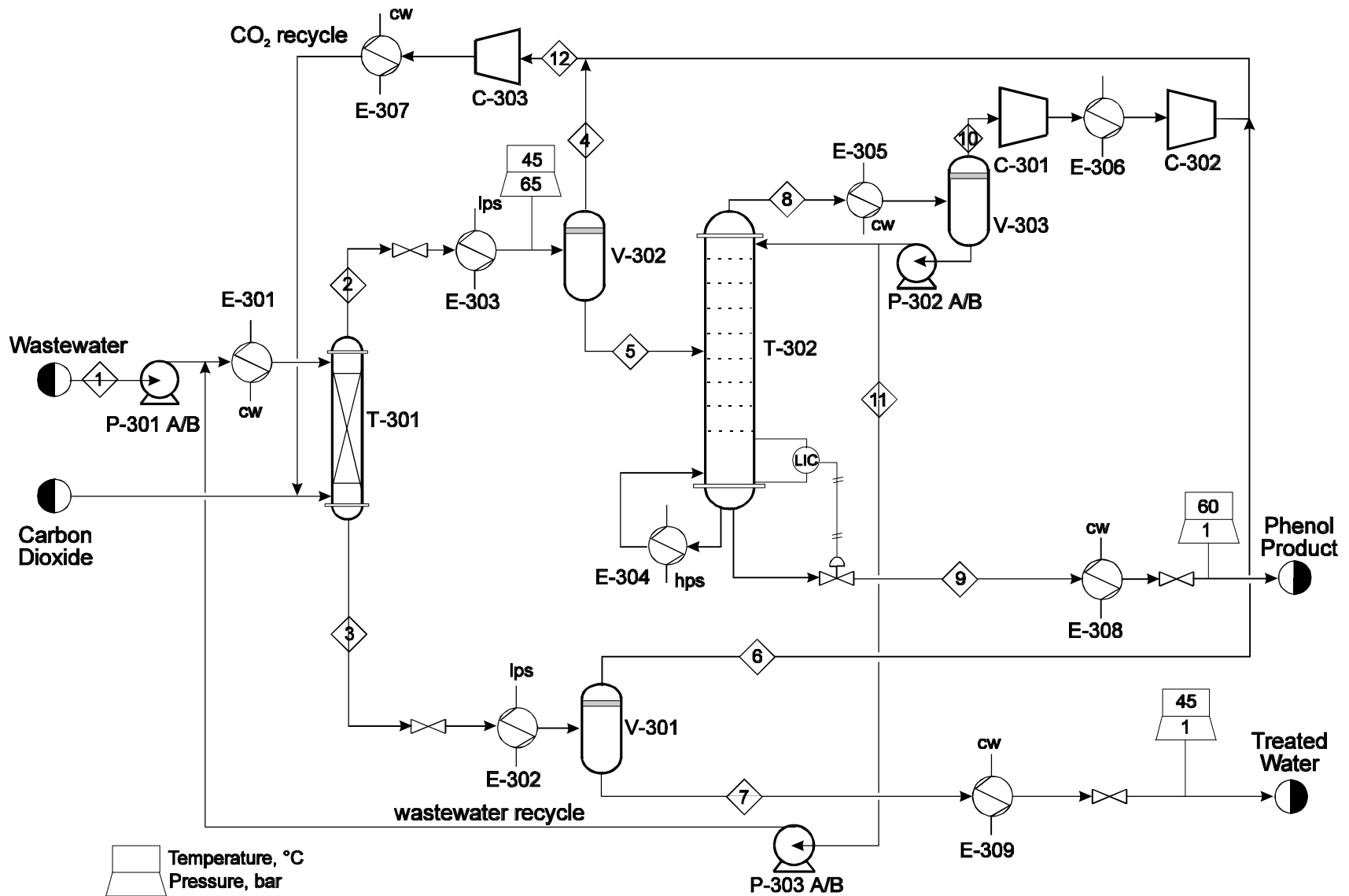
Stream Summary for Phenol Wastewater Treatment with Supercritical CO₂

Stream Number	1	2	3	4	5	6
Temperature (°C)	40					
Pressure (bar)	1					
Vapor Fraction	0.0	sc	sc	1.0	0.0	1.0
Mass Flowrate (kg/h)	10,370	38,860	10,350	37,860	1,000	350
Molar Flowrate (kmol/h)	563	881	564	861	20	8
Component Flowrates (kmol/h)						
carbon dioxide	-	861	8.0	859	2.0	8.0
phenol	7.8	8.1	-	0.3	7.8	-
water	556	11.7	556	1.7	10	-

Stream Number	7	8	9	10	11	12
Temperature (°C)						
Pressure (bar)						
Vapor Fraction	0.0	1.0	0.0	1.0	0.0	1.0
Mass Flowrate (kg/h)	10,000	450	730	90	180	38,300
Molar Flowrate (kmol/h)	556	22	7.8	2	9.9	871
Component Flowrates (kmol/h)						
carbon dioxide	-	2.0	-	2.0	0.02	869
phenol	*		7.8	-	0.01	0.3
water	556	20	**	-	9.9	1.7

* 39 ppb

** $6.22 \cdot 10^{-8}$ kmol/h



PFD for Phenol Wastewater Treatment with Supercritical CO₂