Supercritical Water Oxidation of Phenol Wastewater Stream

Background

The effective removal of organic pollutants from industrial wastewaters is a problem of great importance. Phenol and substituted phenols are common and are priority pollutants because they are suspected carcinogens as well as being extremely toxic to aquatic life and imparting a strong taste and bad odor to water, particularly after chlorination. The main sources of phenolic wastewater are the industries such as petrochemicals, coal gasification, pesticide manufacture, and electroplating and metallurgical operations. In the process considered here, the phenol concentration in water is 6.8 wt%, a typical value for steel coking facilities. The target concentration for effluent water is 39 ppb.

Supercritical water oxidation (SCWO) is being developed as an economically viable and ecologically safe ultimate destruction technology to treat such wastewater streams. The organic pollutants react with oxygen in an aqueous environment at reaction conditions beyond the critical point of water (T_c = 374°C, P_c = 218 bar) to give CO_2 and H_2O as the ultimate products. Supercritical water facilitates dissolution of both organic compounds and oxygen, thereby creating a single homogenous phase for the oxidation.

Environmental Significance

Treatment of a waste stream

Process Description

The PFD is attached. In the process, the wastewater stream, containing 6.8 wt% phenol, is fed into the system as Stream 2. This stream is then pumped up to pressure by pump P-801 A/B. After being pressurized, the wastewater stream is then heated in a fired

heater, H-801, so that it becomes a supercritical fluid. Stream 1, containing 200% excess O_2, is compressed. An alternative design that might me considered would be to use air as the source of oxygen. Stream 3, containing the compressed oxygen is mixed with Stream 5, the supercritical wastewater stream, prior to entering the reactor, R-801. The supercritical effluent stream, Stream 7, contains only carbon dioxide, water, oxygen, and virtually no phenol. This stream is then cooled and partially condensed in a heat exchanger, E-802, before it enters the flash vessel, V-801, where the off-gas is vented to the atmosphere in Stream 9 and the purified water is recovered in Stream 10. After removal of the purified water in the flash vessel, the off-gas in Stream 9 could be recycled to recover the unused O_2.

Necessary Information and Simulation Hints

Water becomes a supercritical fluid (SCF) when heated above its critical temperature pumped above its critical pressure, which are 374°C and 218 bar, respectively. The overall reaction for the complete oxidation of phenol to inorganic products is:

$$C_6H_5OH + 7\ O_2 \rightarrow 6\ CO_2 + 3\ H_2O$$

A rate law for phenol disappearance kinetics valid between 380°C and 480°C has been determined experimentally[1]. The rate law is:

$$\text{rate} = 10^{2.34} \exp(-12.4/RT)[\text{phenol}]^{0.85}[O_2]^{0.50}[H_2O]^{0.42}$$

All simulations were run using SRK for *K* values and enthalpy models.

References

1. Gopalan, Sudhama and Phillip E. Savage. "A Reaction Network Model for Phenol Oxidation in Supercritical Water," *AIChE-Journal*, Vol. 41, No. 8, pp. 1864-1873, 1995.

Equipment Descriptions

C-801 Oxygen Compressor

P-801 A/B Wastewater Pumps

H-801 Wastewater Heater

R-801 Reactor

E-802 Reactor Effluent Cooler

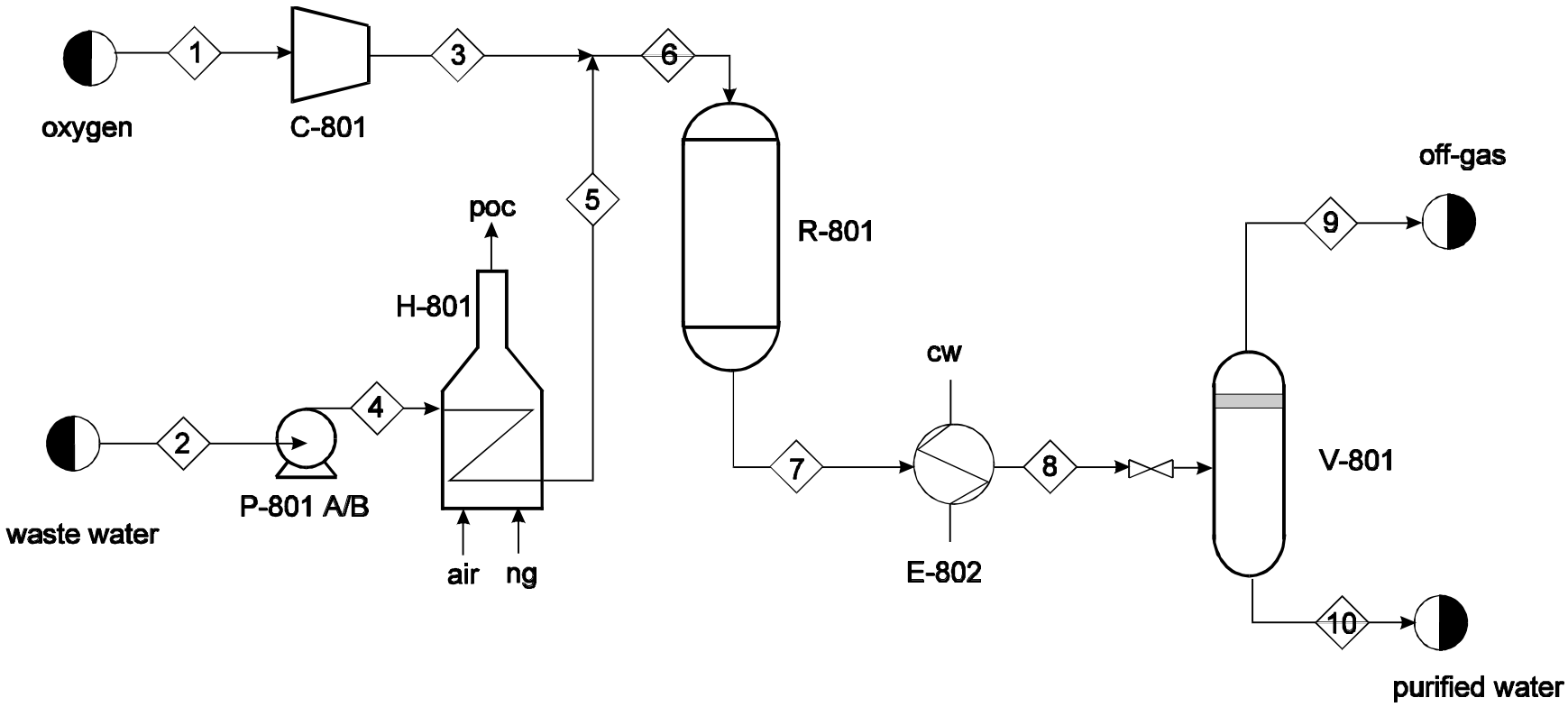
V-801 Flash Vessel

Supercritical Water Oxidation Stream Table

Stream No.	1	2	3	4	5	6
Temperature (°C)	20.00	20.00	420.32	25.84	430.18	400.00
Pressure (bar)	1.01	1.01	250.11	250.00	250.00	250.00
Phase	vapor	liquid	SCF*	liquid	SCF*	SCF*
Total Flow (kg/h)	5218.71	10730.00	5218.71	10730.00	10730.00	15948.71
Total Flow (kmol/h)	163.09	562.85	163.09	562.85	562.85	725.94
Component Flowrates (kmol/h)						
Water	--	555.09	--	555.09	555.09	555.09
Phenol	--	7.76	--	7.76	7.76	7.76
Carbon Dioxide	--	--	--	--	--	--
Oxygen	163.09	--	163.09	--	--	163.09

Stream No.	7	8	9	10
Temperature (°C)	644.77	40.00	40.00	40.00
Pressure (bar)	249.66	248.98	5.00	5.00
Phase	SCF*	V/L mix	vapor	liquid
Total Flow (kg/h)	15948.70	15948.70	5571.58	10377.12
Total Flow (kmol/h)	733.70	733.70	157.67	576.03
Component Flowrates (kmol/h)				
Water	578.36	578.36	2.34	576.03
Phenol	--	--	--	--
Carbon Dioxide	46.54	46.54	46.54	--
Oxygen	108.79	108.79	108.79	--

* Supercritical Fluid



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