

Bench-Scale Design of a Low-Temperature Pyrolysis and Steam Reforming System for the Treatment of Uranium-Bearing Spent TBP

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1. Introduction

In the nuclear chemical industry, a solution of tributyl phosphate (TBP) in kerosene or dodecane is used in the solvent extraction of uranium, plutonium, and thorium from spent nuclear fuel dissolved in nitric acid [1]. Spent TBP, a combustible waste solvent, is not readily incinerated due to problems associated with condensation of phosphoric acid [2, 3]. A two-stage pyrolysis system that consists of a low-temperature pyrolysis at $\leq 450^\circ\text{C}$ and a higher-temperature steam-assisted pyrolysis at $\geq 800^\circ\text{C}$ has been proposed as an alternative oxidation technology for the destruction of spent TBP. Off-gas from this two-stage pyrolysis system includes various unburned hydrocarbons (UHCs) as well as complete-steam reforming products, CO and H_2 , which should be substantially oxidized prior to emission into the atmosphere. Catalytic oxidation is considered as an advantageous and safe treatment method for UHCs [4]. A Pt-based honeycomb monolith is considered to be an effective combustion catalyst for UHCs. Numerous studies on platinum monolith honeycomb reactors have focused on catalytic combustion of a single fuel [5]. The present study investigated the catalytic oxidation of a mixture of various UHCs from the proposed two-stage pyrolysis of waste TBP, in a platinum monolith honeycomb reactor. A wide ranging parametric model study was performed to establish proper conditions of a platinum monolith honeycomb reactor for the bench-scale system design.

2. Methods

The molar concentration of the steam reformer off-gas was first calculated to establish input parameters for the simulation of the catalytic oxidizer. A vertical cylindrical steam reformer with a 10-cm diameter and 30-cm length was assumed as an ideal plug flow reactor (PFR), in which there is no mixing in the axial direction but perfect mixing in the directions traverse this. Calculations for the molar concentration of the steam reformer off-gas were performed with PLUG code in the CHEMKIN 4.11 program package. In the modeling study for the catalytic oxidizer, a honeycomb monolith reactor with a 10-cm diameter and 20-cm length is considered as a special case of a PFR. Input values of honeycomb monolith reactor parameters used for the simulation are shown in Table 1.

Table 1. Honeycomb monolith reactor parameters

Parameters	Input value
Number of cells per square inch, N_{cpsi} (in^{-2})	400
Cell wall thickness, t_w (10^{-3} in)	7
Diameter of monolith reactor, d_r (cm)	10
Length, L_R (cm)	20
Surface density of platinum metal (moles cm^{-2})	2.7E-9
Washcoat thickness, δ (μm)	0.1
Metal dispersion (%)	70
Metal surface area ($\text{cm}^2 \text{g}^{-1}$)	1.89E6
Porosity, ϕ_p (-)	0.85
BET ($\text{m}^2 \text{g}^{-1}$)	25

3. Results and Discussion

Simulated results of steam-assisted high-temperature PFR (ID of 10 cm) with a steam equivalence ratio of 2, which equals to 50% of stoichiometric steam feed rate for complete steam reforming reaction, as a function of temperature are shown in Fig. 1. Temperature appeared to be the most critical operating parameter for the destruction of fed C_4H_8 . At $\geq 900^\circ\text{C}$, a 5cm PFR length is sufficient to substantially decompose C_4H_8 ; however, at 800°C , 15cm PFR length is required. High-temperature steam assisted pyrolysis in a PFR at $\geq 800^\circ\text{C}$ with a length of 30 cm appeared to be capable of destroying UHCs from low-temperature pyrolysis of spent TBP.

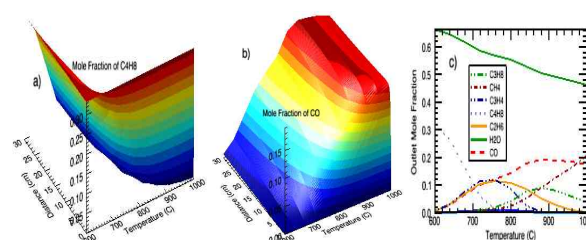


Fig. 1. Simulated results of steam-assisted pyrolysis of butene at $\phi = 2$: (a) butane (b) CO (c) outlet mole fraction of UHCs.

Numerically calculated oxidation efficiency (η) of UHCs at $\phi = 0.2$ and $\text{GHSV} = 1650 \text{ h}^{-1}$ plotted as a function of temperature are shown in Fig. 2(a). Substantial catalytic destruction of UHCs started at about 450°C from a reactor distance of 13 cm. Fig. 2(b) indicates that catalytic oxidation of H_2 , CO, and CH_4 is

extremely fast at $\geq 450^\circ\text{C}$ and they are completely oxidized at $\geq 480^\circ\text{C}$. Oxidation of C_3H_8 and C_2H_6 started at 500°C but their oxidation rate was relatively slow, when compared to that of H_2 , CO and CH_4 . However, several hundred ppms of UHCs remained in the outlet off-gas of the reactor at 800°C . This is due to the generation of C_2H_4 , CH_2O , and CH_2CO from the incomplete oxidation of C_3H_8 and C_2H_6 , as shown in Fig. 1(c).

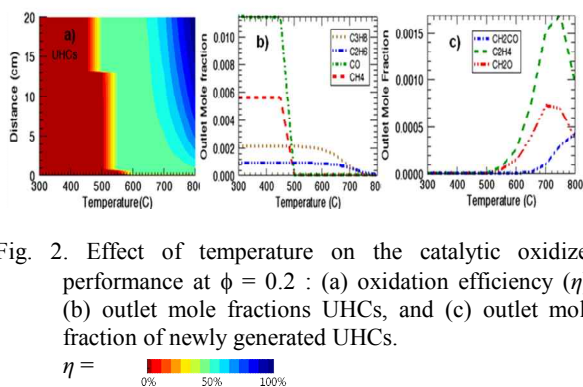
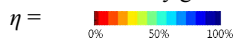


Fig. 2. Effect of temperature on the catalytic oxidizer performance at $\phi = 0.2$: (a) oxidation efficiency (η), (b) outlet mole fractions UHCs, and (c) outlet mole fraction of newly generated UHCs.



The starting temperature of the catalytic oxidation is relatively higher when compared to those at $\lambda=2$. However, catalytic oxidation is significantly high at increased temperatures, as shown in Fig. 2(a). Most UHCs were completely oxidized at 550°C from the reactor distance of ≥ 12 cm. All of the feed UHC species were completely destroyed from a reactor distance of ≥ 12 cm at $\geq 550^\circ\text{C}$, as shown in Fig. 3(b).

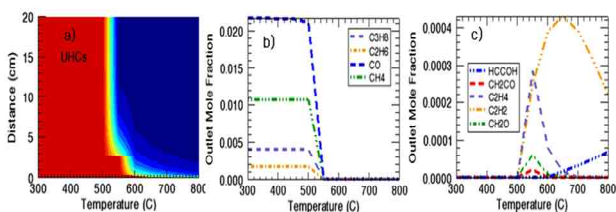


Fig. 3. Effect of temperature on the catalytic oxidizer performance at $\phi = 0.4$: (a) oxidation efficiency (η), (b) outlet mole fraction of feed UHCs, and (c) outlet mole fraction of generated UHCs.

The optimum air equivalence ratio should be established for the combustion of unburned hydrocarbons from waste pyrolysis, etc. Excess air can enhance the oxidation reaction rate at given temperature and gas residence time in a secondary reactor. However, an excessive amount of air reduces the gas residence time as well as the inlet gas temperature, which adversely affects the oxidation reaction performance in a given reactor. It is thus important to determine the optimum oxidizing air feed rate for the oxidation of unburned hydrocarbons in the secondary oxidation

furnace. The optimum temperature of the catalytic oxidizer was determined to be $\geq 550^\circ\text{C}$.

The minimum required temperature for substantial catalytic oxidation was about 550°C . Reduction of ϕ from 1.0 to 0.4 resulted in an increase of UHC destruction efficiency. An increase in the gas flow rate also reduced the oxidation efficiency due to incomplete oxidation of feed UHCs but its influence at higher temperatures above 550°C is small. Finally, the optimum ranges were determined as follows: temperature $\geq 550^\circ\text{C}$, an equivalence ratio of 0.4-0.6. Finally, the bench-scale system was conceptually designed as shown in Fig. 4.

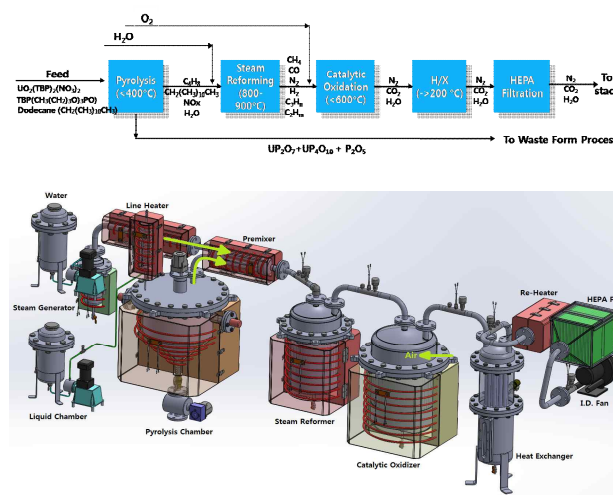


Fig. 4. Process flow diagram (top) and basic design of bench-scale pyrolysis and steam reforming system

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