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Experimental study on thermal hazard of tributyl phosphate-nitric acid mixtures using micro calorimeter technique

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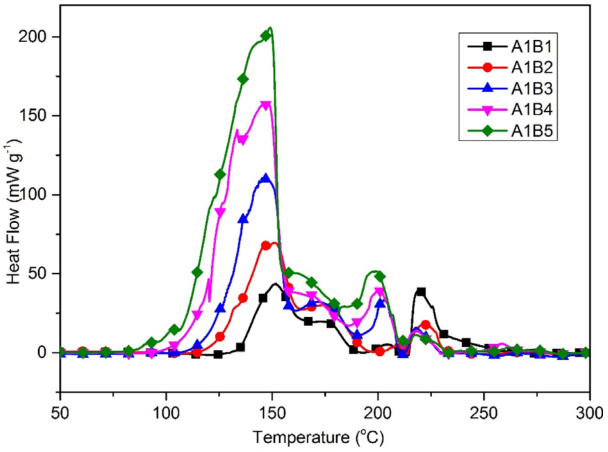
HIGHLIGHTS

- Heat flows after mixing TBP with nitric acid are of different orders of magnitude.
- Thermodynamics and kinetics of tributyl phosphate-nitric acid mixtures are derived.
- Tributyl phosphate directly reacts with nitric acid and form organic red oil.
- Thermal runaway could occur at 79 °C with a high nitric acid concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

During PUREX spent nuclear fuel reprocessing, mixture of tributyl phosphate (TBP) and hydrocarbon solvent are employed as organic solvent to extract uranium in consideration of radiation contaminated safety and resource recycling, meanwhile nitric acid is utilized to dissolve the spent fuel into small pieces. However, once TBP contacts with nitric acid or nitrates above 130 °C, a heavy "red oil" layer would occur accompanied by thermal runaway reactions, even caused several nuclear safety accident. Considering nitric acid volatility and weak exothermic detection, C80 micro calorimeter technique was used in this study to investigate thermal decomposition of TBP mixed with nitric acid. Results show that the concentration of nitric acid greatly influences thermal hazard of the system by direct reactions. Even with a low heating rate, if the concentration of nitric acid increases due to evaporation of water or improper operations, thermal runaway in the closed system could start at a low temperature.

1. Introduction

Extracting uranium and plutonium from spent nuclear fuel and nuclear wastes is a widely used strategy for the safe, permanent, and fuel recycling disposal to radioactive material generated from lab experiments, electronic system, and national defense [1–3].

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Nomenclature

A	Pre-exponential factor (s^{-1})
ARC	Accelerating rate calorimeter
C80	C80 micro calorimeter
DBP	Dibutyl phthalate
dH/dt	Overall heat flow ($J\,g^{-1}$)
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
E_a	Apparent activation energy ($J\,mol^{-1}$)
ΔG°	Free energy (kJ mol-1)
h	Plank constant
ΔH°	Free enthalpy (kJ mol-1)
H_{peak}	Maximum heat flow ($mW\,g^{-1}$)
K_B	Boltzmann constant
M	Mass of reactant (g)
M_0	Initial mass of the reactant (g)
MBP	Monobutyl phthalate
n	Reaction order (dimensionless)
q_G	Heat generation (J)
R	Universal gas constant ($J\,mol^{-1}\,K^{-1}$)
ΔS°	Free entropy ($J\,mol^{-1}\,K^{-1}$)
t	Time (s)
T	Temperature of system (K)
TBP	Tributyl phosphate
T_{end}	End temperature (K)
TG	Thermogravimetry
T_{on}	Onset temperature (K)
T_{peak}	Peak temperature (K)

During extraction performance and speciation of PUREX spent nuclear fuel reprocessing, an organic solvent, mixture of 30 wt% tributyl phosphate (TBP) and 70 wt% hydrocarbon solvent, would be employed to extract uranium in the form of $UO_2(NO_3)_2{\cdot}2TBP$ [4]. During PUREX, some diluents, like *n*-dodecane and kerosene, are used to depress the maximum metal loading of TBP [5], while nitric acid is utilized to dissolve the spent fuel into small pieces [3]. Once TBP contacts with nitric acid or nitrates above 130 °C, they react to form a heavy "red oil" layer with accompanying high pressure and thermal runaway reactions [5–12]. These hazards are fatal to nuclear laboratory or factory, which may cause explosion accident and radiation contaminated pollution. Several accidents caused by PUREX have been reported in history, among which major ones are listed in Table 1 [13–15].

Thermal decomposition pathways of TBP and formation mechanism of red oil have been reported by previous studies. Smitha et al. applied an ARC (accelerating rate calorimeter) to study TBP decomposition behavior under adiabatic conditions [16]. TBP showed multiple self-heating exothermic reactions with onset temperature 251.5 °C. The thermal behavior of TBP followed first-order Arrhenius kinetic model with three stages. First, TBP decomposes into dibutyl phthalate (DBP) from 251.5 to 255.5 °C and produces gaseous butane. Then, DBP decomposes into monobutyl phthalate (MBP) and releases butane from 280 to 422.8 °C. Finally, MBP decomposed into phosphoric acid at 430.8 °C. In another study, they investigated the thermal hazards of 30 wt% TBP, 70 wt% *n*-dodecane and different concentration nitric acid. It was hypothesized that oxidation of butanol to botanic acid was the main cause of exothermic behavior [17]. Chandran et al. used ARC and DSC (differential scanning calorimetry) to study the thermal decomposition of neat TBP, acid-solvate, and solutions of TBP in diluents under air atmosphere [18]. A mixture of constant boiling composition of 15.6 mol L^{-1} nitric acid and TBP was found to have runaway reaction at 89 °C. Patil et al. developed a novel methodology by using a flow reactor, through which information of liquid and gaseous products during thermal decomposition could be obtained [19]. It was suggested that, from 130 to 180 °C, thermal decomposition of TBP-nitric acids mixture system was an irreversible first order reaction. However, Chapman and Robinson found that at elevated temperatures, the decomposition of TBP, diluent, and nitric acid proceed to release heat under high heating rate [20,21]. Temperature of liquid mixture would increase, which would also promote the reaction rate and show an autocatalytic phenomenon.

According to previous studies, few attentions were paid to investigations and comparisons of thermal behavior for each chemical and their mixtures, especially their sensitivity to thermal runaway hazards of the mixture at elevated temperatures. The thermal behavior in reprocessing is a very complex phenomenon, depending upon the type and amount of diluents, concentration of nitric acid, and the proportion and so on [22]. These chemicals exist mostly in evaporator or other closed equipment during reprocessing, so it is necessary to explore their thermal behavior in a closed system. To the best of present authors' knowledge, very few microcalorimeter tests have been carried out, especially tests focusing on the sensitivities to each other or to the mixture system at elevated temperatures.

C80 micro calorimeter has been widely used for thermal analysis, including spontaneous behavior of coal stockpile [23,24] and stored wet cotton [25], thermal stabilities of lithium ion batteries [26,27], and possible catalytic effects of some annexing agents [28]. Many optional temperature programming could be set, such as isothermal scanning mode, constant heating rate mode, and step scanning mode [29–31]. The basic principle of C80 is similar to DSC, but it has merits of higher sensitivity (10^{-6} μW) and ability to hold gram level liquid or solid substances [32].

Thermal decomposition of tributyl phosphate, mixed with nitric acid at elevated temperatures, would be the trigger of runaway reactions in nuclear fuel reprocessing plants [17,33–35], in which

Table 1
Accidents involving tributyl phosphate (TBP) and nitric acid in spent fuel reprocessing.

Number	Time	Site	Facility	Components	Result
1	January 12, 1953	Savannah River Plant, USA	Pilot batch evaporator	36.1 L of TBP adduct	Explosion of evaporator into pieces, and strong damage of building
2	February 5, 1953	Hanford, USA	Pilot batch evaporator	From 12 to 40L TBP	Rapid pressure in evaporator
3	November 20, 1959	Oak Ridge, USA	Pilot continuous evaporator	TBP or Turco 4501	Radioactive contamination of neighboring buildings and a cost of $10,000 and 335,000 for repair and deactivation
4	February 12, 1975	Savannah River Plant, USA	Full-scale boiler-type batch denitrator	120L of TBP with uranyl nitrate	Explosion and destruction of denigrator room at cost of $230,000-300,000
5	July 16, 1980	Ontario, USA	Full-scale evaporator	TBP-kerosene mixture	Explosion and damage of equipment
6	April 1993	Tomsk-7, Russia	Temperature and pressure control were working	A Layer of nitric acid (14.2 mol L^{-1}, V = 1.5 m^3)	Pressure up to 17 at, explosion and secondary explosion o released products, substantial damage to equipment and radiative contamination of 135 km^2